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THE STRUCTURE OF CRYSTALS

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BY

RALPH W. G. WYCKOFF

American Chemical Society
Monograph Series

BOOK DEPARTMENT

The CHEMICAL CATALOG COMPANY, *Inc.*

19 EAST 24TH STREET, NEW YORK, U. S. A.

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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (*a*) Scientific and (*b*) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

The development of knowledge in all branches of science, and especially

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in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coördinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large

part upon the measure of coöperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

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Preface

From time to time in the past possible arrangements which would not conflict with the known chemical properties, or with cleavage, symmetry, etc., have been proposed for the atoms (or molecules) in crystals. The discovery of the diffraction of X-rays and the presentation of a plausible theory correlating these diffraction effects with atomic positions have made available much additional information upon which to base suggestions as to the atomic arrangements prevailing in crystals. All of the earlier and many of the present crystal structures based upon X-ray data have this quality of *suggested* solutions of questions of atomic grouping.

The use of the theory of space groups puts a different aspect upon the problem of atomic arrangement. It is the virtue of this theory that with its aid crystal structures can be *deduced* from a group of postulates of generally admitted validity. When the particular conditions of the individual problem permit the collection of enough data, the only possible atomic arrangement compatible with these postulates can be obtained; if the data are insufficient for this purpose all of the conceivable crystal structures which remain experimentally indistinguishable are completely known. The present monograph aims to outline the methods of crystal structure deduction as they now exist and to treat the available diffraction data from the more exacting standpoint they make possible.

The very fact that this enlarged subject of crystal analysis draws its methods of attack from several of the old sciences introduces a serious difficulty into its adequate presentation; among these older sciences it is now more or less of an outcast. Most chemists seem to find in the purely physical means of experimentation and in the introduction of theoretical crystallography a proof that it does not belong to chemistry; for many physicists it is difficult to believe that the physical processes alone are insufficient; and crystallography (as distinct from mineralogy), to which crystal analysis is in many ways most closely related, is practically nonexistent in this country. Consequently in presenting this book as a Monograph of the American Chemical Society the writer has endeavored to reduce analytical complexities to a minimum [for instance by deducing expressions for only the simplest (cubic) crystals] and to stress thereby only the necessary underlying assumptions. The greatest difficulty in crystal analysis is the problem of thinking clearly in three dimensions. For most of us this is surmounted only by practise and it is the writer's belief that the greatest aid to this end is the extensive use of graphical methods and of figures: usually the study of a figure will make a relation clearer than pages of description. For this purpose and to keep the first

part within the confines of a treatise of interest to chemists, the text has been abbreviated as much as is consistent with clearness and extensive use has been made of diagrams and figures. Also because of the varied trainings of the persons now interested in the results of crystal structure studies it has been necessary to introduce brief discussions of the physical properties of X-rays and the symmetry properties of crystals which to students trained in these fields must seem superfluous; an effort has been made in treating of these matters to include only the most necessary topics.

Two attempts, for the most part independent of each other, have been made to develop a science of crystal analysis. The one which provides the point of view for this book arose from the early attempts of S. Nishikawa to use the theory of space groups in studies of crystal structure; the other, which antedates in many of its phases the first, has grown up on the continent of Europe through the efforts of P. P. Ewald,[1] R. Gross, P. Niggli and others. Different European investigators use different analytical methods; the fundamental assumptions are essentially the same, however, and it does not appear that anything but confusion would be the practical result of discussing in this monograph each individual procedure. Except where better or supplementary methods have been adopted bodily (with due recognition) alternative procedures will be referred to only in footnotes or in the bibliography.

It is thus clear that this monograph makes no pretense at being a handbook in the sense of providing an account of all of the various methods of crystal structure study which have been proposed and used. It is rather intended to give (in Part I) the reaction of a single point of view towards the material of crystal analysis as it now exists. All of the tools that are available are here considered but all of the different ways of using them are not touched upon. It is the purpose of the second part to treat all existing diffraction data from the point of view outlined in Part I. This is not done in an entirely satisfactory manner, partly because of the limitations of time and space, partly because of the labor involved in reworking the published data from this standpoint and partly because enough data have not in many instances been published. The writer hopes that most diffraction experiments have been included in Part II; he would greatly appreciate having omissions brought to his attention. No data published after January 1, 1924, are included in this book.

Information from crystal analysis has already thrown light upon many problems of both a theoretical and a practical interest. An adequate discussion of these applications is only possible after crystal structure knowledge itself has been put upon a well-defined basis; at the same time such a discussion would have so many ramifications in different branches of science that it could not be short. For these reasons no effort has been made to do more than catalogue the various uses thus far made of X-ray

[1] Since this book was written a monograph on crystal analysis has been published by P. P. Ewald (Kristalle u. Röntgenstrahlen, Berlin, 1923). Though different phases of the subject are stressed in the two books, a similar point of view actuates both.

diffraction data for other purposes than determinations of atomic arrangement and to treat, in only the briefest and most incomplete fashion, a few topics of especial concern to chemists.

The author wishes to take this opportunity of expressing his gratitude to his teacher and friend, Dr. Shoji Nishikawa, for the great benefits received through early association with him in the study of crystals, to Dr. H. E. Merwin, who has given much of his time and especially of his interest to problems of crystal analysis that have arisen from time to time, to Professor William Duane, who in examining this book for the Board of Editors has made many valuable suggestions, to Dr. A. L. Day and Dr. R. B. Sosman for kindly reading the manuscript, and to Dr. A. L. Day and the Carnegie Institution of Washington for the opportunity of presenting this monograph as a publication of the Geophysical Laboratory.

RALPH W. G. WYCKOFF.

Geophysical Laboratory,
January, 1924.

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Table of Symbols

The following symbols are frequently used in this book:

A° = Angstrom unit = 1×10^{-8} cm.

a : b : c is the axial ratio of a crystal. The letters a, b and c are also used to designate unit lengths along the axes of reference.

a_0, b_0, c_0 are the lengths of the sides of the unit cell of a crystal as measured along the X-, Y- and Z- axes of coördinates respectively.

α, β, γ are the axial angles of a crystal.

c′ is the velocity of light.

d_{hkl} = the spacing of geometrically like planes parallel to the possible crystal face (hkl).

(hkl) = the Miller indices of a possible crystal face. For a hexagonal crystal the Miller-Bravais indices are (hkil).

hkl(n) = the Miller indices of a reflection from a plane (hkl) in the nth order.

h′ = Planck's constant.

θ = the angle of reflection for X-rays. The deviation of a diffracted beam of X-rays is 2θ.

κ = absorption constant.

λ = wave length.

I = intensity.

I_0 = original intensity.

M = weight of a chemical molecule.

M′ = molecular weight.

m = number of chemical molecules within the unit cell of a crystal.

μ = absorption coefficient.

μ_a = atomic absorption coefficient.

μ'/ρ = "true" mass absorption coefficient.

N = number of electrons in an atom. It equals the atomic number of an uncharged atom.

$\overline{N}$ = the scattering power of an atom containing N electrons. It is to be taken as approximately equal numerically to N itself.

N′ = the number of atoms in the gram atom = 6.06×10^{23}.

n = the order of reflection.

ν = frequency.

r = radius of sphere of projection.

ρ = density.

V = the volume of the unit cell of a crystal.

V' = potential (in volts).

x', y', z' are the cartesian coördinates of a point.

$x = x'/a_0$; $y = y'/b_0$; $z = z'/c_0$.

PART I

THE METHODS OF CRYSTAL ANALYSIS

THE STRUCTURE OF CRYSTALS

Chapter I. The Symmetry Characteristics of Crystals

Upon the basis of an atomic theory the atoms or molecules of a body which is maintaining its own shape unchanged (a non-viscous "solid") will move in closed paths about fixed equilibrium positions. Two distinct types of such "solids" can be imagined: In one these equilibrium positions possess a special regularity in arrangement, in the other no such order exists. The first may be called *crystalline*, the latter lies in the class of *amorphous* materials. A crystalline body throughout which this order is undisturbed constitutes a single *crystal*.

The External Symmetry of Crystals [1]

Elements of Symmetry.—A large class of solid bodies, met in nature or prepared in the laboratory, have properties which appear to justify their classification as crystalline substances. Individual crystals, thus found, are more or less perfectly formed polyhedrons. Their fundamental symmetry characteristics are shown by a study of the distribution of their plane faces and of various physical properties, such as refractive indices, which are unlike in different directions. In this way the following elements of symmetry, and these only, have been recognized as present in crystals.

Axes of Symmetry.—If in a figure a rotation about some line combined with a translation along it leaves the figure in its original geometrical aspect the figure is said to have a screw axis of symmetry. If the amount

[1] The external symmetry properties of crystals and the methods of their investigation are treated in a large number of crystallographic and mineralogical texts. Among the more comprehensive of these may be named:

1. E. S. Dana (W. F. Ford, reviser), Textbook of Mineralogy (Wiley, 1922).
2. A. E. H. Tutton, Crystallography and Practical Crystal Measurement, 2 Volumes (London, 1922).
3. P. Groth, Physikalische Krystallographie, 4th Edition (Leipzig, 1905); Elemente der physikalischen und chemischen Krystallographie (München, 1921).
4. P. Niggli, Lehrbuch der Mineralogie (Berlin, 1920).

These books are more or less typical of different points of view from which the questions of crystal symmetry are commonly approached.

of the translation is zero the symmetry axis is a simple rotational axis of symmetry. The following screw and rotation axes are observed in crystals: 360° (one-fold), 180° (two-fold), 120° (three-fold), 90° (four-fold) and 60° (six-fold) axes (Figures 1 and 2).

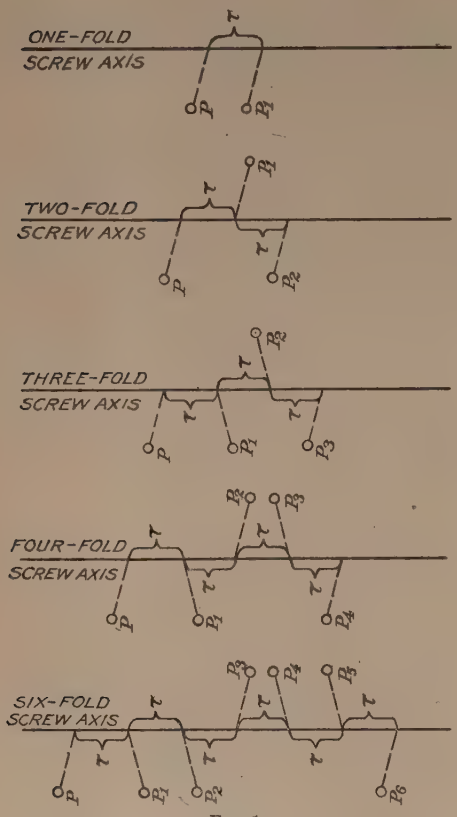


Fig. 1

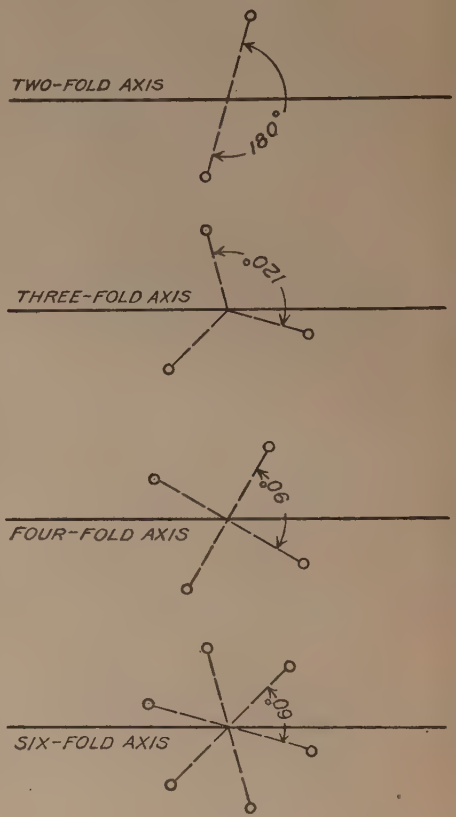


Fig. 2

Fig. 1.—The crystallographically possible screw axes of symmetry.

Fig. 2.—The crystallographically possible rotational axes of symmetry. Since a rotation of 360° brings a figure back to its original aspect, every body will also contain an infinite number of such one-fold rotational axes.

Planes of Symmetry.—In Figure 3 the line POP′ is perpendicular to the plane ABCD and meets it in the point O. If P′O = OP, P and P′ stand in a mirror image relation to each other. Any plane that can be passed through a figure so that every point upon one side of the plane has a corresponding point on the opposite side in a mirror image relation to it is a plane of symmetry. If a figure can be brought into geometrical coincidence with itself by a reflection combined with a translation of definite mag-

nitude and direction (Figure 4) in a plane, the latter is a glide plane of symmetry. A rotation about an axis combined with a reflection in a plane perpendicular to the axis constitutes a rotary-reflection.

Centers of Symmetry.—A point is a center of symmetry if a line drawn from any point of the figure to it and extended an equal distance beyond encounters a point corresponding to the arbitrarily chosen point (Figure 5). A rotary-inversion consists of a rotation of definite angle about an axis followed by an inversion through a point in the axis. If this axis is one-fold the resulting symmetry operation is obviously the same as a simple inversion; if it is two-fold, the operation is identical with a reflection in a plane normal to the axis.

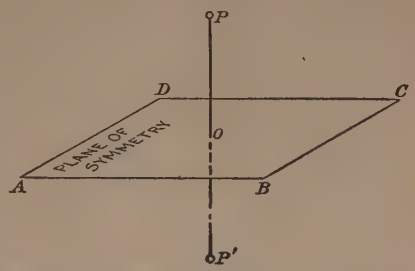


FIG. 3.—The line POP′ is perpendicular to ABCD. If P′O = PO, P and P′ are in a mirror image relation to one another.

The Point Groups.[1]—It can be shown that there are but 32 distinctive ways of taking these elements of symmetry singly and of combining them

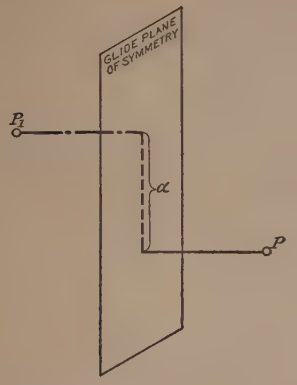


FIG. 4.—A glide plane of symmetry.

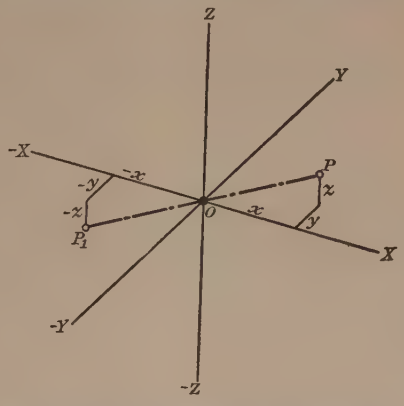


FIG. 5.—O is the center of symmetry of a figure in which P and P_1 are any corresponding points.

together. The point groups, or classes of crystal symmetry, thus formed may be uniquely defined either by stating their symmetry properties or, more analytically, by giving the coördinates of the *equivalent points* which

[1] A deduction of the point groups is given in all books which develop the theory of space groups (as well as numerous others). See for instance:

1. A. Schoenflies, Krystallsysteme und Krystallstruktur (Leipzig, 1891).
2. H. Hilton, Mathematical Crystallography (Oxford, 1903); and especially
3. A. Schoenflies, Theorie der Kristallstruktur (Berlin, 1923).

arise from any arbitrarily chosen point by the operation of each of their elements of symmetry. On the basis of the kind of axes of reference necessary for their description the point groups themselves can be divided into seven systems identical with the crystallographic systems of symmetry.

It is desirable to have some means of illustrating in two dimensions the characteristics of crystals. Several types of projection have been used for this purpose. Two of them, the stereographic and gnomonic, have proved of value in X-ray crystal analysis and will be considered at a later point (Chapter IV). The former is useful, however, in showing graphically the symmetry of the crystal classes. In doing this the intersections of elements of symmetry upon a circumscribed sphere are projected upon the plane of a great circle of the sphere through the extremities of the perpendicular diameter [1] (Figure 6). The position of any point (such as

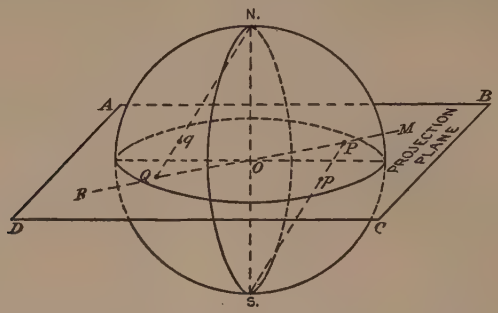


FIG. 6.—If M is some point above the plane of the great circle perpendicular to the diameter NS, its stereographic projection is p. This point is obtained by drawing MO and then the straight line PpS where P is the intersection of MO with the sphere of projection and p is the intersection of PS with the plane. The stereographic projection of a point R below the plane of projection is a similar intersection q of the line QN with the plane.

an equivalent point of a point group) can be shown by drawing a line from it to the center of the sphere and projecting its intersection with the surface in the usual manner (thus M of Figure 6 is projected upon ABCD at the point p). If the projected point lies in the upper hemisphere it is marked by a cross (x); if in the lower, by a circle (o). In showing the symmetry properties of a crystal class it is customary to take the plane of the projection normal to the principal symmetry axis. Such projections are shown in figures which accompany the subsequent descriptions of the point groups. In these diagrams the ends of 2-, 3-, 4- and 6-fold rotation axes will be designated by , , , and , those of 4- and

[1] Used in this way the stereographic projection is often called Gadolin's projection.

6-fold screw axes by and ; planes of symmetry will be shown as full lines; dotted lines, in so far as they do not coincide with the two-fold axes, are merely construction lines.

The symmetry of the crystal classes with their analytical expressions are briefly as follows:

I. Triclinic System: Groups requiring as coördinate axes for their description any three lines of unequal unit lengths making any angles with one another (Figure 7).

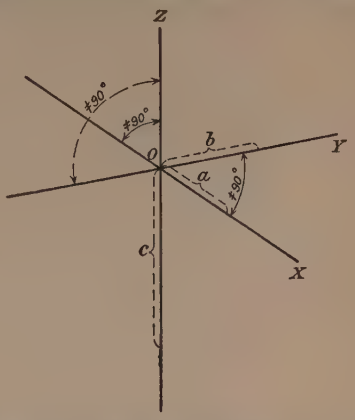
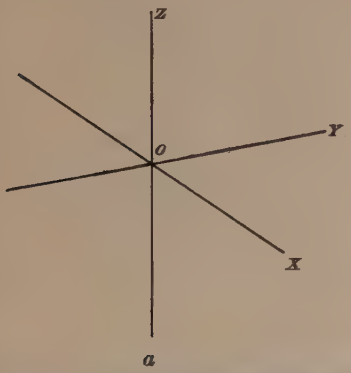
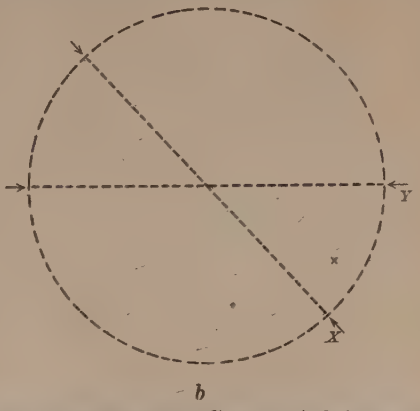


FIG. 7.—The axes of reference of point groups belonging to the triclinic system. The three axes are of unequal unit lengths ($a \neq b \neq c$) and make any angles with one another.

Point group 1C, (C_1) [Hemihedral class].[1] The only elements of symmetry possessed by this group are an infinite number of one-fold (360° −) axes of symmetry (Figure 8, *a* and *b*). It is evident that the operation of any one of these axes upon any point xyz will bring it into coincidence with itself. This single set of coördinates, xyz, thus is an adequate analytical description of the characteristics of this class of symmetry.



a



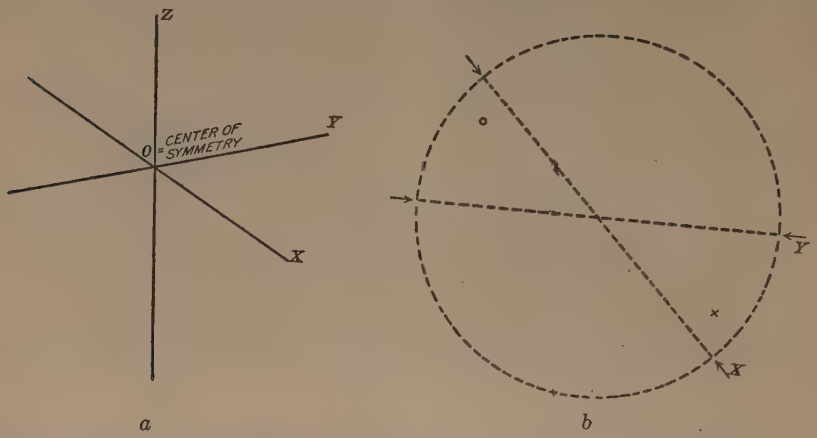
b

FIG. 8*a*.—The only symmetry properties of the point group 1C are an infinite number of one-fold rotational axes of which any three may in general be taken as axes of reference.

FIG. 8*b*.—The stereographic projection of the point group 1C. Every point is unlike every other point.

[1] The point (and space) group symbols to be used have been described by R. W. G. Wyckoff, Am. J. Sci., *6*, 288 (1923). Those in parentheses are the usual ones of Schoenflies.

Point group 1Ci, (C_i) [Holohedral class]. Besides the one-fold axes possessed by the previous class, and all other classes, a center of symmetry



a *b*

FIG. 9*a*.—The center of symmetry characteristic of 1Ci is taken at the intersection of the triclinic axes of reference.

FIG. 9*b*.—The stereographic projection of the two equivalent points of the point group 1Ci.

is present (Figure 9, *a* and *b*). If this point is placed at the origin of the coördinate axes, the point $-x-y-z$ [1] will be geometrically equivalent to the point xyz. Consequently the symmetry properties of this group are described by the two sets of coördinates of the points (the *equivalent points*) obtained one from the other by the operation of the symmetry element of the group: $xyz;\ \bar{x}\bar{y}\bar{z}$.

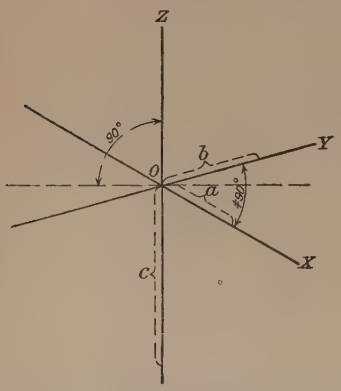


FIG. 10.—The axes of reference for the monoclinic point groups are of unequal unit lengths ($a \neq b \neq c$). Z is perpendicular to the plane of X and Y which, however, can make any angle with one another.

II. Monoclinic System: Groups requiring as coördinate axes for their description three lines of unequal unit length one of which (the Z-axis) is perpendicular to the plane of the other two, which make any angle with one another (Figure 10).

Point group 2c, (C_s) [Hemihedral class]. This group is characterized by a single plane of symmetry which must be the plane containing the X- and Y-axes (Figure 11, *a* and *b*). Since the operation of a plane of symmetry which contains two

[1] It is the uniform practise in writing coördinate values to place minus signs over the letters to which they apply. Thus $-x$ is $\bar{x}$, $-y$ is $\bar{y}$, etc.

axes of coördinates and is perpendicular to the third is always to change the sign of the third coördinate value, the point xyz̄ is equivalent to xyz. These two sets of coördinates then furnish an analytical description of the symmetry of the group.

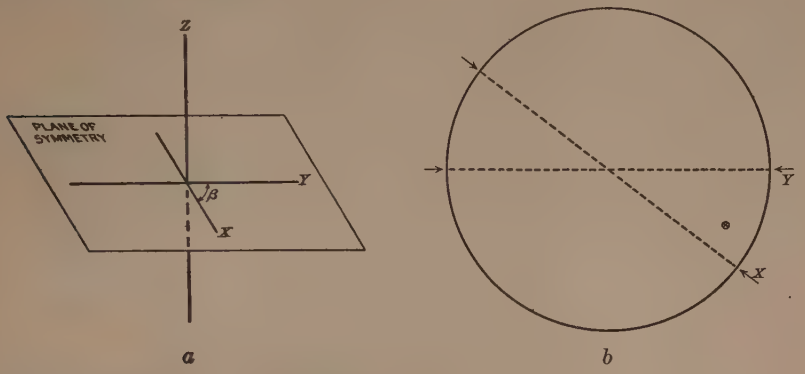


FIG. 11*a*.—The symmetry properties of the point group 2c.

FIG. 11*b*.—The stereographic projection of the symmetry properties and equivalent points of the point group 2c. The plane of projection is coincident with the plane of symmetry.

Point group 2C, (C_2) [Hemimorphic hemihedral class]. This group possesses a single two-fold axis of symmetry which is to be taken as coincident with the Z-axis of coördinates (Figure 12, *a* and *b*). Since by the

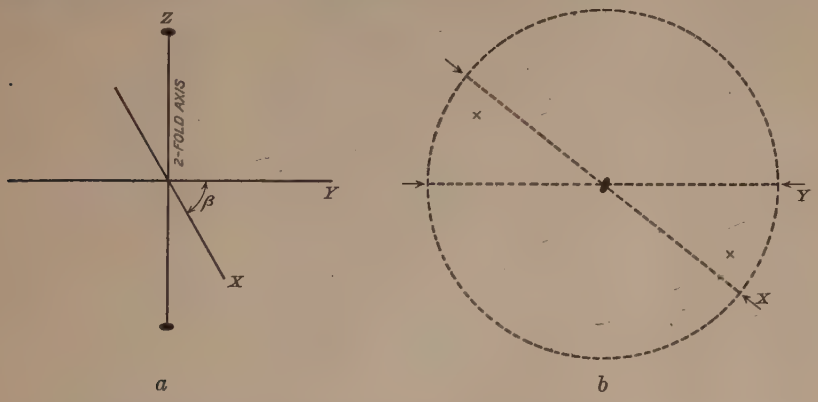
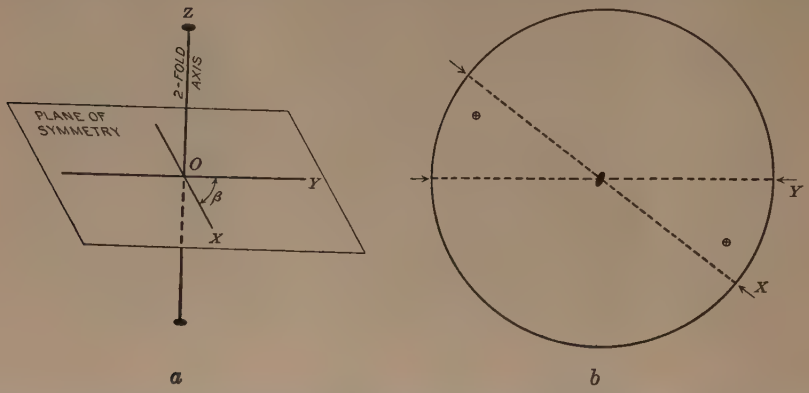


FIG. 12*a*.—The symmetry properties of the point group 2C.

FIG. 12*b*.—The stereographic projection of the two-fold axis of symmetry and of equivalent points of the point group 2C.

operations of this axis there always will be a point x̄ȳz geometrically equivalent to xyz, these two sets of coördinates provide an analytical description of this group.

Point group 2Ci, (C_2^h) [Holohedral class]. This class is characterized by a two-fold axis and a plane of symmetry located as shown in Figure 13, *a* and *b*. From the preceding descriptions it is evident that the four points



a *b*

FIG. 13*a*.—The symmetry properties of the point group 2Ci. The two-fold axis and perpendicular plane of symmetry also make O a center of symmetry.
FIG. 13*b*.—The stereographic projection of the point group 2Ci.

xyz; $\bar{x}\bar{y}z$; $xy\bar{z}$; $\bar{x}\bar{y}\bar{z}$ are all equivalent. A glance either at Figure 13 or at these coördinates shows that the two elements of symmetry also combine in placing a center of symmetry at the origin of coördinates.

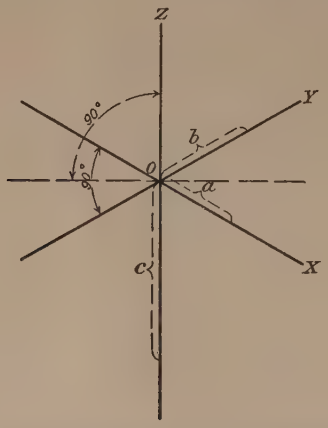


FIG. 14.—The axes of reference of the orthorhombic point groups. The three axes of unequal unit lengths ($a \neq b \neq c$) are mutually perpendicular.

III. Orthorhombic System: Groups requiring as coördinate axes for their description three lines of unequal unit lengths perpendicular to one another (Figure 14).

Point group 2e, (C_2^v) [Hemimorphic hemihedral class]. The symmetry elements of this class are a two-fold axis and a plane of symmetry arranged as shown in Figure 15, *a* and *b*. The four equivalent points are readily seen to be: xyz; $\bar{x}\bar{y}z$; $\bar{x}yz$; $x\bar{y}z$.

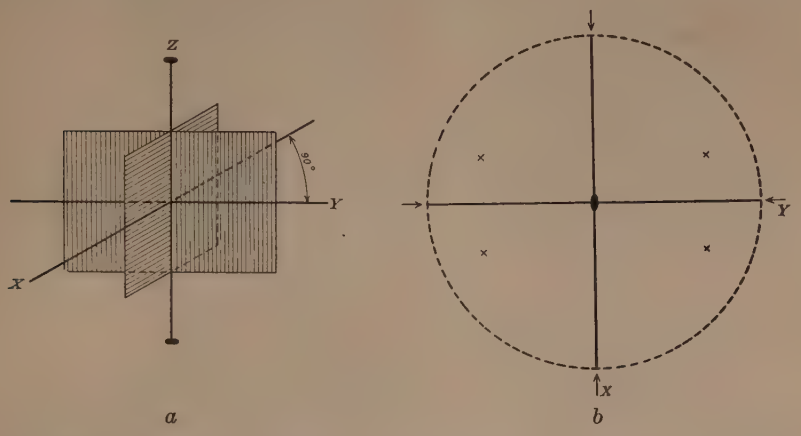


FIG. 15*a*.—The symmetry properties of the point group 2e. If the plane of X and Z is taken as the plane of symmetry it will be seen that the operation of this plane combined with that of the two-fold axis lying in it, makes the perpendicular YZ plane also a plane of symmetry.

FIG. 15*b*.—The stereographic projection of the point group 2e.

Point group 2D, (V) [Enantiomorphic hemihedral class]. The three mutually perpendicular two-fold axes (Figure 16, *a* and *b*) of this class yield the equivalent points: xyz; $x\bar{y}\bar{z}$; $\bar{x}y\bar{z}$; $\bar{x}\bar{y}z$.

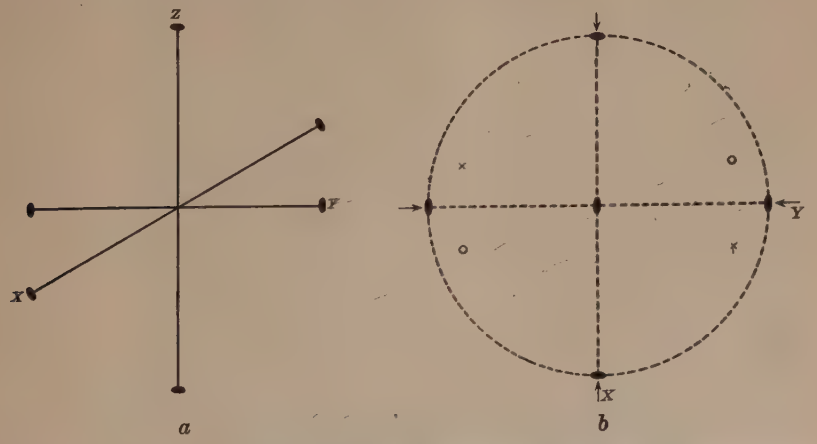
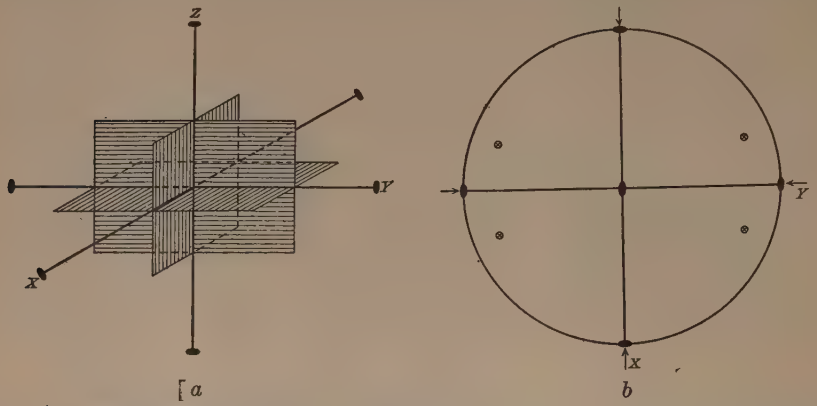


FIG. 16*a*.—The three mutually perpendicular two-fold axes of the point group 2D.

FIG. 16*b*.—The stereographic projection of the point group 2D.

Point group 2Di, (V^h) [Holohedral class]. To this group belong three two-fold axes and a plane of symmetry coincident with the plane of two of them (Figure 17). As with 2Ci, this combination of two-fold axis and



a b

FIG. 17*a*.—The symmetry properties of the point group 2Di. The three mutually perpendicular two-fold axes and the plane of symmetry coincident with the plane of two of them introduce the two other symmetry planes shown in this figure.

FIG. 17*b*.—The stereographic projection of the point group 2Di.

normal plane of symmetry places a center of symmetry at the origin. The coördinates of the equivalent points are:

$$xyz;\ x\bar{y}\bar{z};\ \bar{x}y\bar{z};\ \bar{x}\bar{y}z;\ \bar{x}\bar{y}\bar{z};\ \bar{x}yz;\ x\bar{y}z;\ xy\bar{z}.$$

IV. Tetragonal System: Groups requiring as coördinate axes for their description three lines perpendicular to one another, the unit length of two being equal but different from that of the third (Figure 18).

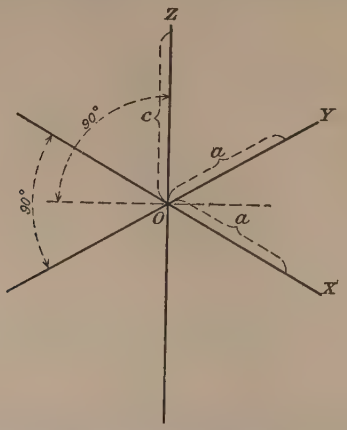


FIG. 18.—The axes of reference of the tetragonal point groups. The unit length along X and Y is different from that along Z ($a \neq c$).

Point group 4c, (S_4) [The tetartohedral class of the second sort]. The single element of symmetry of this group is a four-fold axis of rotary reflection, the plane of the reflection being that of the X- and Y- axes (Figure 19, *a* and *b*).[1] The four equivalent points are: xyz; $\bar{y}x\bar{z}$; $\bar{x}\bar{y}z$; $y\bar{x}\bar{z}$.

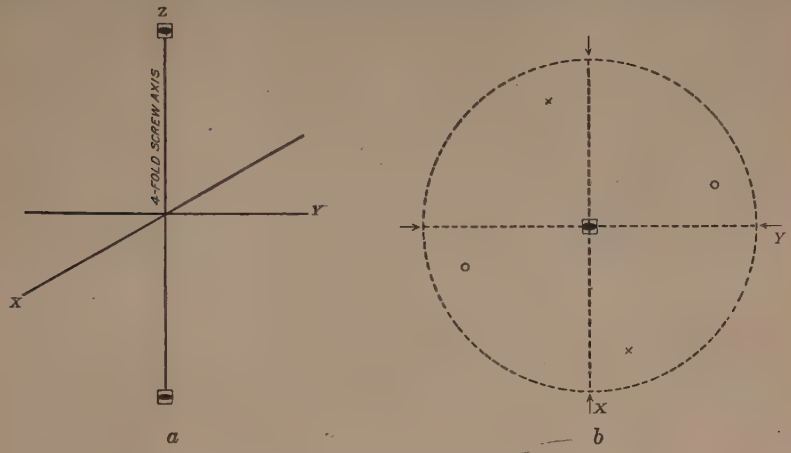


FIG. 19*a*.—The symmetry properties of the point group 4c.
FIG. 19*b*.—The stereographic projection of the point group 4c.

Point group 4C, (C_4) [Tetartohedral class]. The coördinates of the four equivalent points arising from the single four-fold axis (Figure 20, *a* and *b*) are: xyz; $\bar{y}xz$; $\bar{x}\bar{y}z$; $y\bar{x}z$.

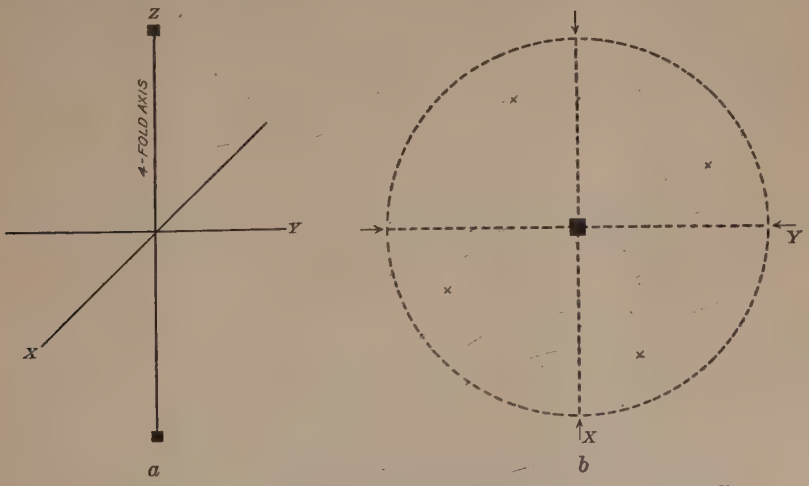
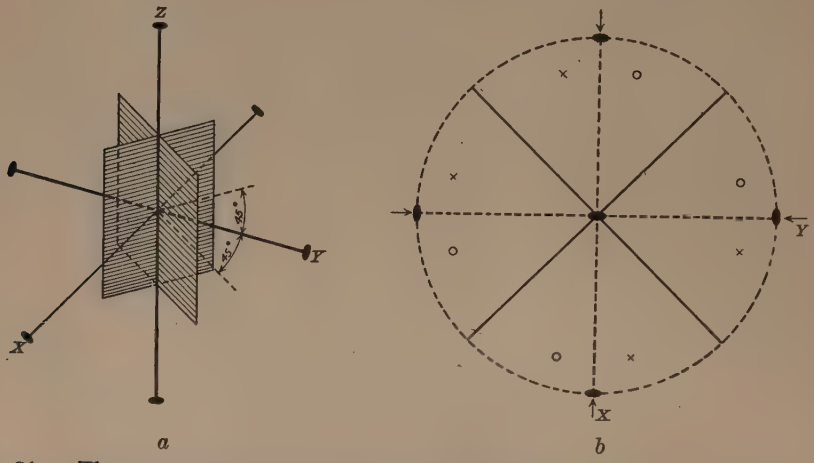


FIG. 20*a*.—The single four-fold rotation axis of the point group 4C.
FIG. 20*b*.—The stereographic projection of the point group 4C.

[1] As Figure 19*b* suggests, the symmetry element of this group can also be taken as a four-fold screw axis.

Point group 4d, (V^d) [Hemihedral class of the second sort]. The elements of symmetry are three mutually perpendicular two-fold axes and planes of symmetry in the positions of Figure 21, *a* and *b*. The coördinates of the eight equivalent points are:

$$xyz;\ x\bar{y}\bar{z};\ \bar{x}y\bar{z};\ \bar{x}\bar{y}z;\ yxz;\ \bar{y}x\bar{z},\ y\bar{x}\bar{z};\ \bar{y}\bar{x}z.$$

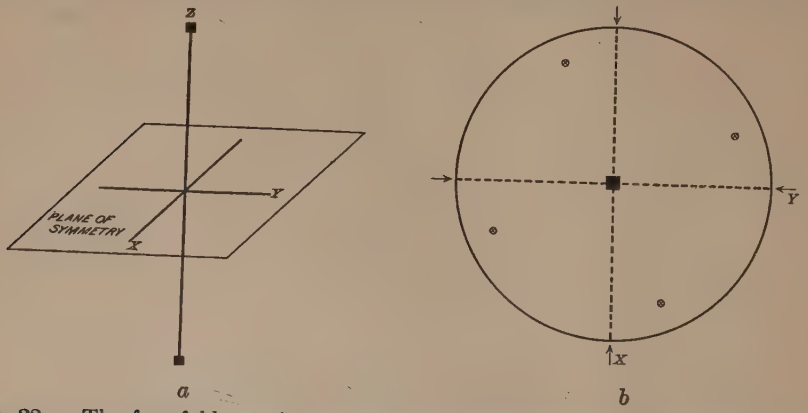


a *b*

FIG. 21*a*.—The symmetry properties of the point group 4d.

FIG. 21*b*—The stereographic projection of the symmetry properties and equivalent points of the point group 4d.

Point group 4Ci, (C_4^A) [Paramorphic hemihedral class]. The positions of the four-fold rotation axis and the reflecting plane perpendicular to it are shown in Figure 22, *a* and *b*. Since the operations of a 90°-axis include



a *b*

FIG. 22*a*.—The four-fold rotation axis and perpendicular plane of symmetry of the point group 4Ci.

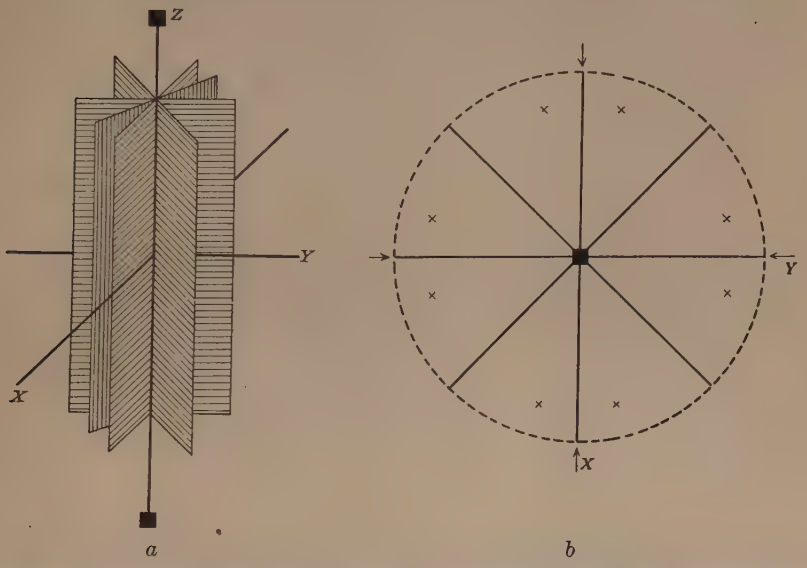
FIG. 22*b*.—The stereographic projection of the point group 4Ci.

those of a 180°-axis the elements of symmetry of this group make the origin a center of symmetry. The equivalent points are:

$$xyz;\ \bar{y}xz;\ \bar{x}\bar{y}z;\ y\bar{x}z;\ \bar{x}\bar{y}\bar{z};\ y\bar{x}\bar{z};\ xy\bar{z};\ \bar{y}x\bar{z}.$$

Point group 4e, (C_4^v) [Hemimorphic hemihedral class]. The four-fold axis and reflecting plane of this group have the positions shown in Figure 23, *a* and *b*. The coördinates of equivalent points are:

$$xyz;\ \bar{y}xz;\ \bar{x}\bar{y}z;\ y\bar{x}z;\ \bar{x}yz;\ yxz;\ x\bar{y}z;\ \bar{y}\bar{x}z.$$



a *b*

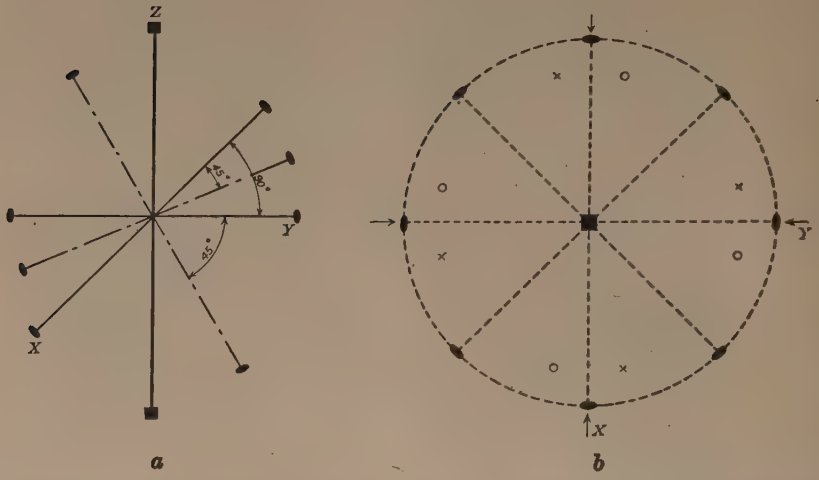
FIG. 23*a*.—The four-fold axis and "vertical" reflecting planes of the point group 4e.
FIG. 23*b*.—The stereographic projection of the point group 4e.

Point group 4D, (D_4) [Enantiomorphic hemihedral class]. The single four-fold axis and the four coplanar two-fold axes perpendicular to it are illustrated in Figure 24, *a* and *b*. The coördinates of the eight equivalent points are:

$$xyz;\ \bar{y}xz;\ \bar{x}\bar{y}z;\ y\bar{x}z;\ x\bar{y}\bar{z};\ \bar{y}\bar{x}\bar{z};\ \bar{x}y\bar{z};\ yx\bar{z}.$$

Point group 4Di, (D_4^h) [Holohedral class]. This class possesses the symmetry elements of the preceding one (4D) together with a plane of symmetry which is coincident with the plane of the two-fold axes (Figure 25, *a* and *b*). As before, the four-fold axis and the reflecting plane normal to it make the origin of coördinates a center of symmetry. The coördinates of the equivalent points are:

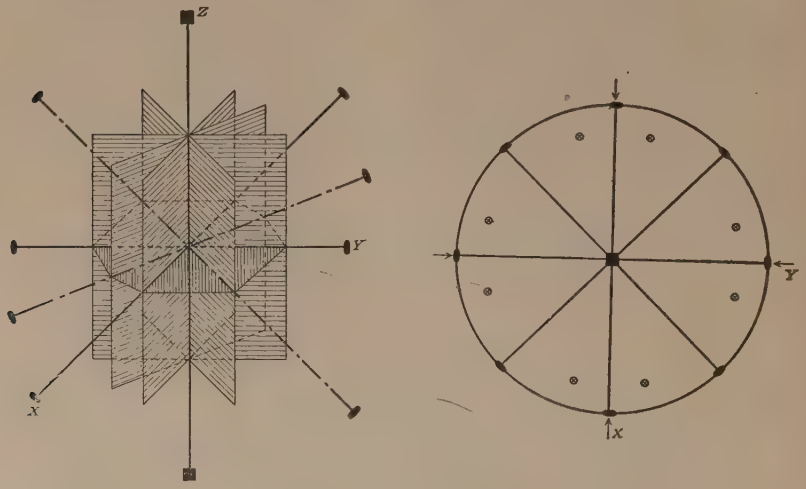
$$xyz;\ \bar{y}xz;\ \bar{x}\bar{y}z;\ y\bar{x}z;\ x\bar{y}\bar{z};\ \bar{y}\bar{x}\bar{z};\ \bar{x}y\bar{z};\ yx\bar{z};$$
$$\bar{x}\bar{y}\bar{z};\ y\bar{x}\bar{z};\ xy\bar{z};\ \bar{y}x\bar{z};\ \bar{x}yz;\ yxz;\ x\bar{y}z;\ \bar{y}\bar{x}z.$$



a *b*

FIG. 24*a*.—The four-fold principal axis and the four co-planar two-fold axes perpendicular to it that are possessed by the point group 4D.

FIG. 24*b*.—The stereographic projection of the point group 4D.



a *b*

FIG. 25*a*.—The symmetry properties of the point group 4Di.

FIG. 25*b*.—The stereographic projection of the point group 4Di.

V. Cubic System: Groups requiring as coördinate axes for their description three mutually perpendicular lines of equal unit lengths (Figure 26).

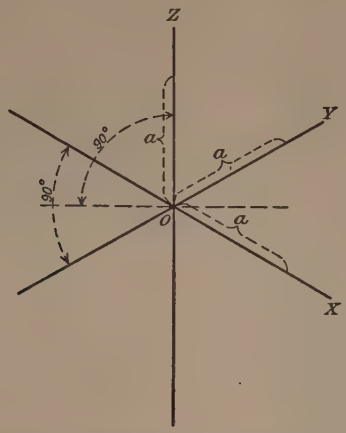
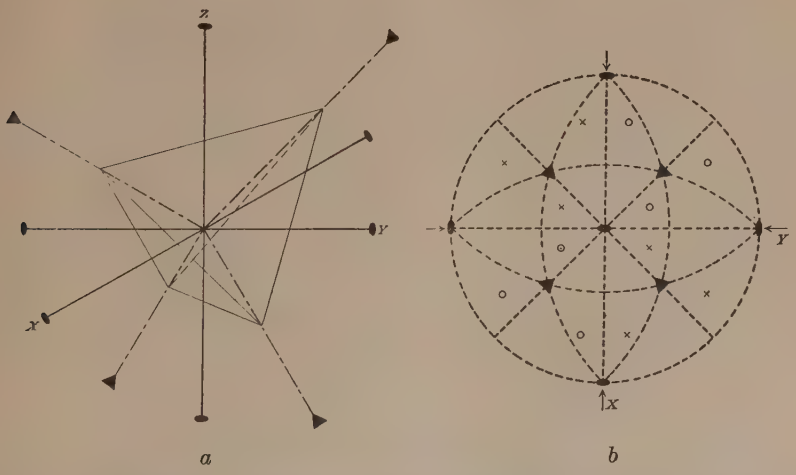


FIG. 26.—The axes of reference of the cubic point groups are three mutually perpendicular lines of equal unit lengths.

Point group T, (T) [Tetartohedral class]. The three two-fold and four three-fold axes of this group have the distribution of Figure 27*a*.



a *b*

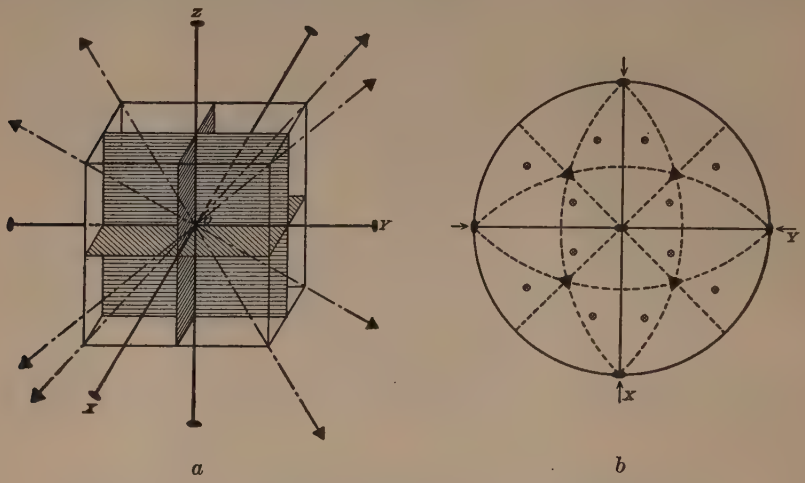
FIG. 27*a*.—The elements of symmetry of the point group T are four three-fold and three two-fold rotation axes which pass through the corners and opposite edges respectively of a circumscribed tetrahedron.

FIG. 27*b*.—The stereographic projection of the point group T.

The coördinates of its 12 equivalent points, common to all cubic point groups, are:

(I) xyz; $x\bar{y}\bar{z}$; $\bar{x}y\bar{z}$; $\bar{x}\bar{y}z$;
zxy; $\bar{z}x\bar{y}$; $\bar{z}\bar{x}y$; $z\bar{x}\bar{y}$;
yzx; $\bar{y}\bar{z}x$; $y\bar{z}\bar{x}$; $\bar{y}z\bar{x}$.

Point group Ti, (T^h) [Paramorphic hemihedral class]. The elements of symmetry of this group are those of the group T and planes of symmetry in the positions of Figure 28, *a* and *b*. It will be observed that two-



a *b*

FIG. 28*a*.—The symmetry properties of the point group Ti.
FIG. 28*b*.—The stereographic projection of the point group Ti.

fold axes and planes of symmetry have the relative positions necessary to make the origin a center of symmetry. The coördinates of equivalent points are those of (I), (point group T) and (II).

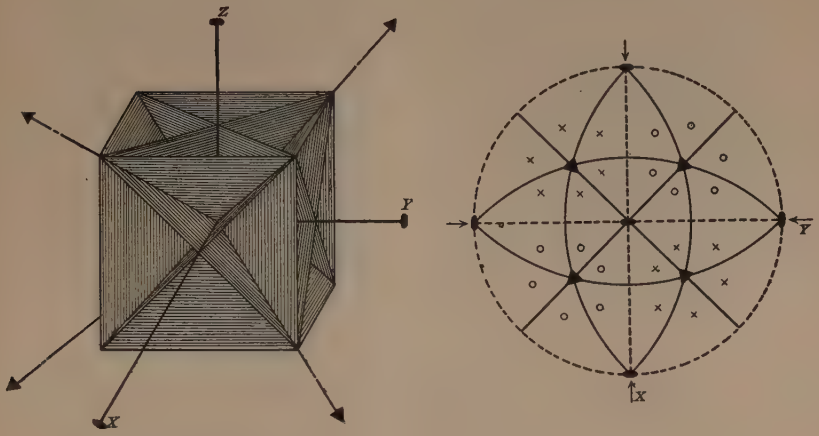
(II) $\bar{x}\bar{y}\bar{z}$; $\bar{x}yz$; $x\bar{y}z$; $xy\bar{z}$; $\bar{z}\bar{x}\bar{y}$; $z\bar{x}y$; $zx\bar{y}$; $\bar{z}xy$; $\bar{y}\bar{z}\bar{x}$; $yz\bar{x}$; $\bar{y}zx$; $y\bar{z}x$.

Point group Te, (T^d) [Hemimorphic hemihedral class]. The elements of symmetry of this class are also those of T and planes of symmetry having the positions of Figure 29, *a* and *b*. The coördinate positions of the equivalent points are those of (I) and the following:

(III) yxz; $\bar{y}x\bar{z}$; $y\bar{x}\bar{z}$; $\bar{y}\bar{x}z$; xzy; $x\bar{z}\bar{y}$; $\bar{x}\bar{z}y$; $\bar{x}z\bar{y}$; zyx; $\bar{z}\bar{y}x$; $\bar{z}y\bar{x}$; $z\bar{y}\bar{x}$.

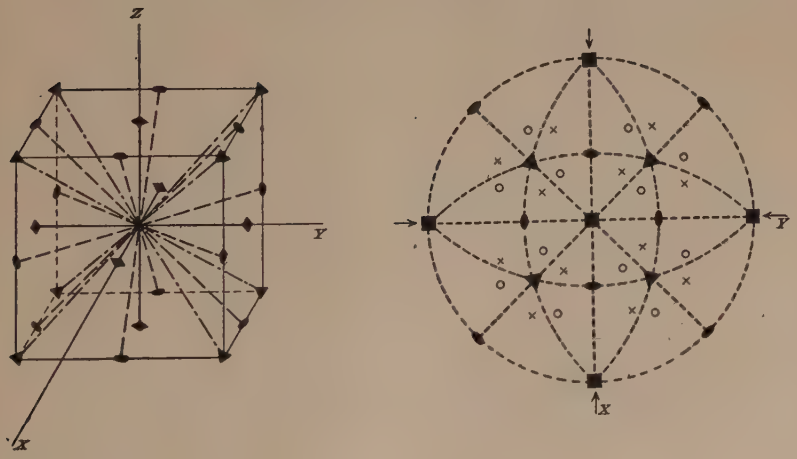
Point group O, (O) [Enantiomorphic hemihedral class]. The three four-fold, four three-fold and six two-fold axes of this group have the distribution shown in Figure 30, *a* and *b*. The coördinate positions of the equivalent points are those of (I) and the following:

(IV) $\bar{y}\bar{x}\bar{z}$; $y\bar{x}z$; $\bar{y}xz$; $yx\bar{z}$; $\bar{x}\bar{z}\bar{y}$; $\bar{x}zy$; $xz\bar{y}$; $x\bar{z}y$; $\bar{z}\bar{y}\bar{x}$; $zy\bar{x}$; $z\bar{y}x$; $\bar{z}yx$.



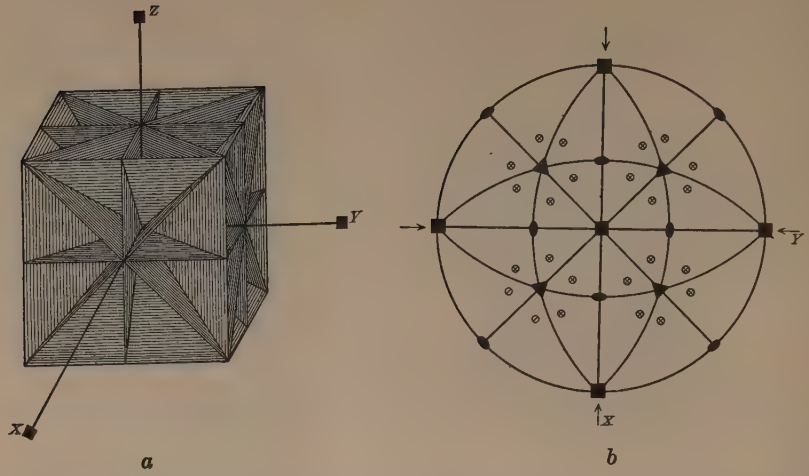
a b

FIG. 29a.—The symmetry properties of the point group Te.
FIG. 29b.—The stereographic projection of the point group Te.



a b

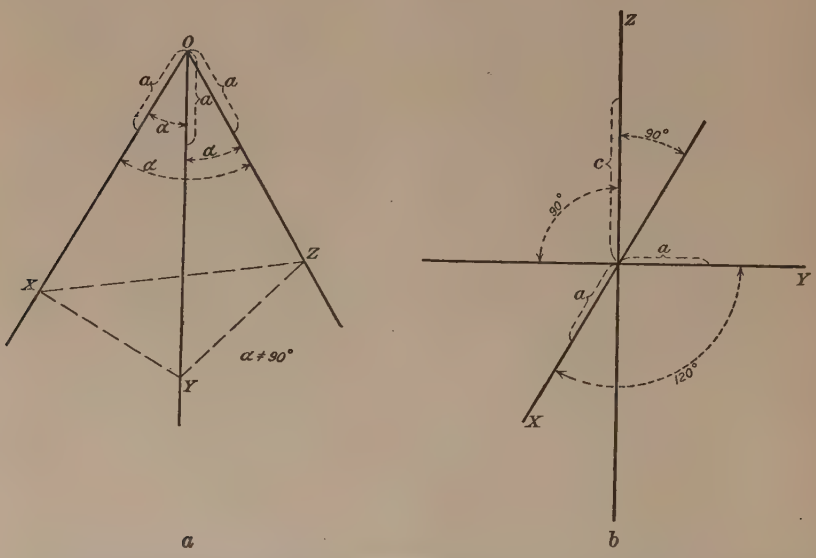
FIG. 30a.—The symmetry properties of the point group O.
FIG. 30b.—The stereographic projection of the point group O.



a *b*

FIG. 31*a*.—The planes of symmetry of the point group Oi. The axes of symmetry (except for the three four-fold axes reproduced also in this figure) are shown in Fig. 30a.

FIG. 31*b*.—The stereographic projection of all of the symmetry properties and of equivalent points of the point group Oi.



a *b*

FIG. 32*a*.—The rhombohedral axes of reference for point groups having the symmetry of the rhombohedral division of the hexagonal system. The three axes are of equal unit lengths and make equal angles ($\alpha \neq 90°$) with one another.

FIG. 32*b*.—The hexagonal axes of reference. Two of these axes (X and Y) are of equal unit lengths and make 120° with one another; the third (Z) is of a different unit length and is normal to the plane of the first two.

Point group Oi, (O^h) [Holohedral class]. The elements of symmetry of this group are those of O (Figure 30) together with reflection planes in the positions of Figure 31*a*. Again these elements of symmetry make the origin a center of symmetry. The coördinates of equivalent points are those of (I), (IV), (II), and (III).

VI. Rhombohedral Division of the Hexagonal System. The point groups of this division are best described in terms of two sets of coördinate axes, (1) rhombohedral axes and (2) hexagonal axes. The rhombohedral axes consist of three lines of equal unit lengths making equal angles one with another (Figure 32 *a*). As hexagonal reference axes are to be chosen two lines of equal unit lengths making 120° with one another and a third axis of different length perpendicular to the plane of the first two.

Point group 3C, (C_3) [Tetartohedral class]. The position of the single three-fold axis of this class in relation to the two sets of reference axes is shown in Figure 33, *a* and *b*. The coördinates of the equivalent points are:

For (1): xyz; zxy; yzx.
For (2): xyz; y − x, $\bar{x}$, z; $\bar{y}$, x − y, z.

Point group 3Ci, (C_3^i) [Hexagonal tetartohedral class of the second sort]. The positions of the three-fold axis and center of symmetry of this group are shown in Figure 34, *a*, *b*, and *c*. The coördinates of equivalent points are:

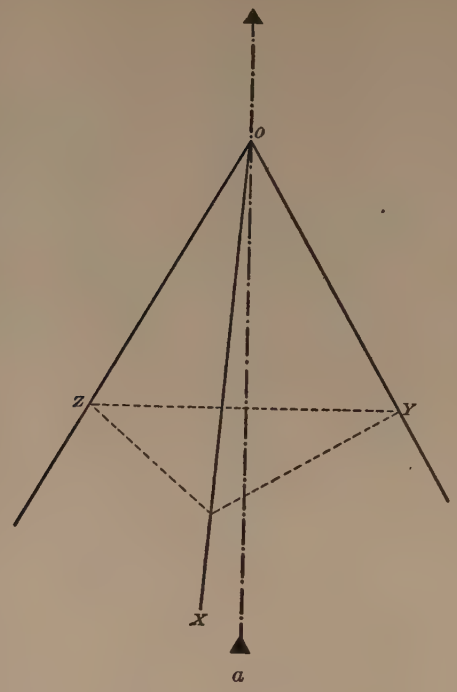
For (1): xyz; zxy; yzx; $\bar{x}\bar{y}\bar{z}$; $\bar{z}\bar{x}\bar{y}$; $\bar{y}\bar{z}\bar{x}$.
For (2): xyz; y − x, $\bar{x}$, z; $\bar{y}$, x − y, z; $\bar{x}\bar{y}\bar{z}$; x − y, x, $\bar{z}$; y, y − x, $\bar{z}$.

Point group 3e, (C_3^v) [Hemimorphic hemihedral class]. The positions of the three-fold axis and the vertical reflecting planes are shown in Figure 35, *a*, *b*, and *c*. Coördinates of equivalent points are:

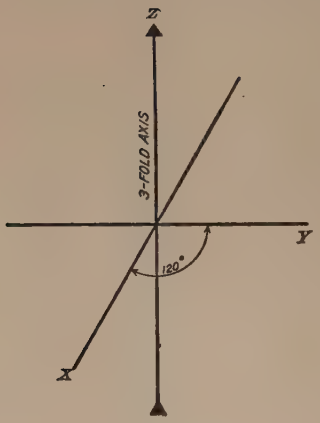
For (1): xyz; zxy; yzx; yxz; xzy; zyx.
For (2): xyz; y − x, $\bar{x}$, z; $\bar{y}$, x − y, z; x − y, $\bar{y}$, z; yxz; $\bar{x}$, y − x, z.

If, as is convenient for some purposes, the vertical reflecting plane is chosen to make an angle of 30° with the X-axis of set (2), slightly different coördinate values will result.[1]

[1] It is a common crystallographic procedure, particularly in this country, to use such oblique axes for rhombohedral and hexagonal groups. Care must therefore be taken in actual practise to avoid confusion.



a



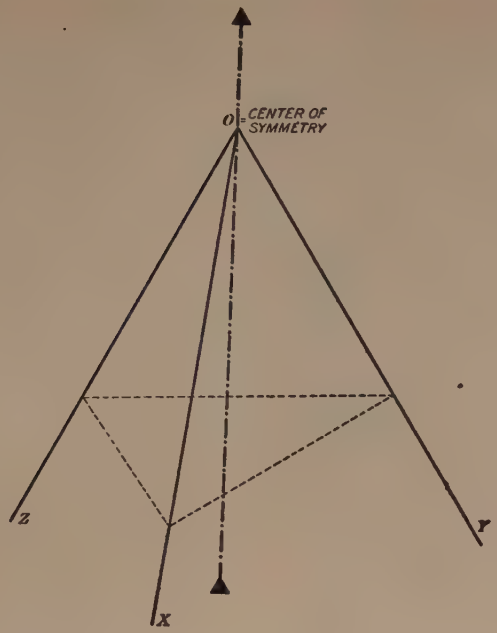
b

c

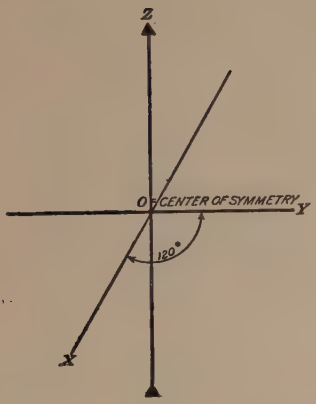
FIG. 33*a*.—The single three-fold axis of the point group 3C is symmetrically placed with respect to the three rhombohedral axes of reference.

FIG. 33*b*.—The single three-fold axis of the point group 3C coincides with the Z hexagonal axis of reference.

FIG. 33*c*.—The stereographic projection of the point group 3C. The positions of hexagonal coördinate axes are shown in this figure.



a



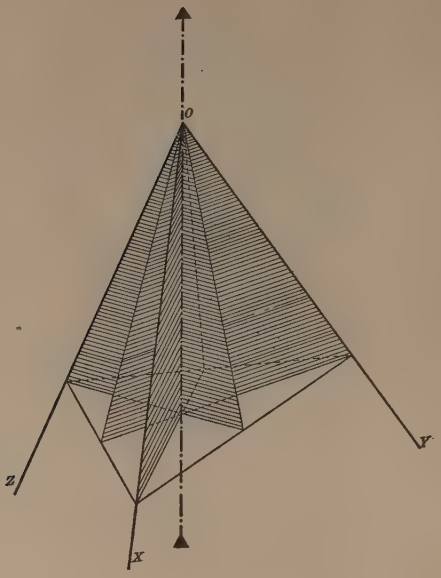
b

c

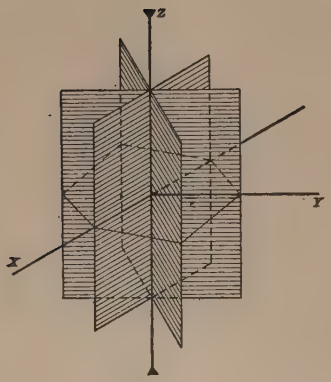
FIG. 34*a*.—The relation of the symmetry elements of the point group 3Ci to the rhombohedral axes of reference.

FIG. 34*b*.—The relation of the symmetry elements of the point group 3Ci to the hexagonal axes of reference.

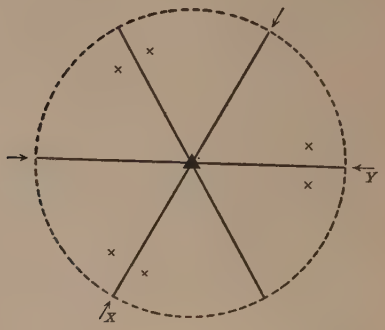
FIG. 34*c*.—The stereographic projection of the point group 3Ci. The positions of hexagonal coördinate axes are shown in this figure.



a



b



c

FIG. 35*a*.—The relation of the symmetry properties of the point group 3e to the rhombohedral axes of reference.

FIG. 35*b*.—The relation of the symmetry properties of the point group 3e to the hexagonal axes of reference.

FIG. 35*c*.—The stereographic projection of the point group 3e. The positions of hexagonal axes of reference are shown in this figure.

Point group 3D, (D_3) [Enantiomorphic hemihedral class]. The distribution of the principal three-fold rotation axis and the three two-fold axes normal to it is shown in Figure 36, *a* and *b*. Their relation to the

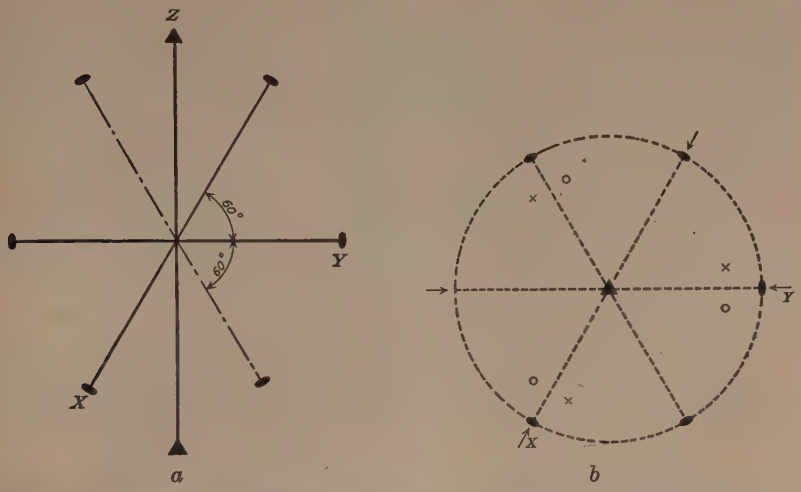


FIG. 36*a*.—The three coplanar two-fold axes of the point group 3D are normal to the three-fold axis. As the figure shows, this principal axis coincides with the hexagonal Z-axis of reference.

FIG. 36*b*.—The stereographic projection of the point group 3D. The positions of hexagonal axes of reference are shown in this figure.

rhombohedral coördinate axes is the same as that of the corresponding elements in Figure 37 *a*. The coördinates of the equivalent points are:

For (1): xyz; zxy; yzx; $\bar{y}\bar{x}\bar{z}$; $\bar{x}\bar{z}\bar{y}$; $\bar{z}\bar{y}\bar{x}$.

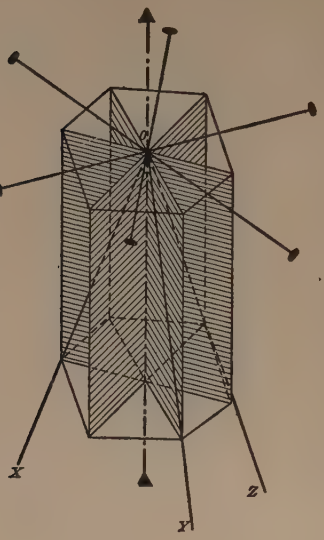
For (2): xyz; $y-x, \bar{x}, z$; $\bar{y}, x-y, z$; $x-y, \bar{y}, \bar{z}$; $yx\bar{z}$; $\bar{x}, y-x, \bar{z}$.

Slightly different coördinates for (2) result from placing the two-fold axes in positions 30° from those of Figure 36 *a*.

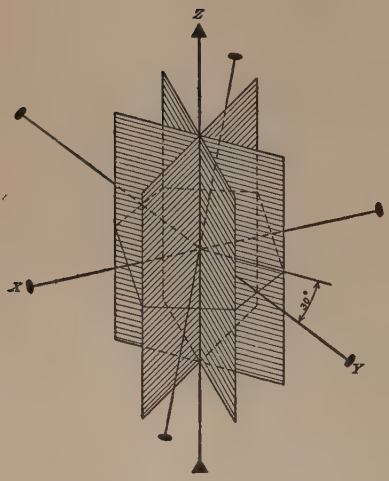
Point group 3Di, (D_3^d) [Holohedral class]. The elements of symmetry of this group are those of 3D together with vertical reflecting planes which bisect the angles between two of the 180°-axes after the manner of Figure 37, *a*, *b*, and *c*. Since this furnishes again the combination of a two-fold axis perpendicular to a reflecting plane the origin will be a center of symmetry. The coördinates of equivalent points are:

For (1): Those of 3D and
$\bar{x}\bar{y}\bar{z}$; $\bar{z}\bar{x}\bar{y}$; $\bar{y}\bar{z}\bar{x}$; yxz; xzy; zyx.

For (2): Those of 3D and
$\bar{x}\bar{y}\bar{z}$; $x-y, x, \bar{z}$; $y, y-x, \bar{z}$; $y-x, y, z$; $\bar{y}\bar{x}z$; $x, x-y, z$.



a



b

c

FIG. 37*a*.—The symmetry properties of the point group 3Di referred to the rhombohedral axes of reference.

FIG. 37*b*.—The symmetry properties of the point group 3Di referred to the hexagonal axes of reference.

FIG. 37*c*.—The stereographic projection of the point group 3Di. The positions of hexagonal axes of reference are shown in this figure.

As before the choice of a direction for the two-fold axes which is turned 30° with respect to that of Figure 37 *b* would lead to different coördinates.

VII. Hexagonal Division of the Hexagonal System. The groups of the division will be described only in terms of the hexagonal axes (Figure 32 *b*).

Point group 6c, (C_{3^h}) [Trigonal paramorphic hemihedral class]. The elements of symmetry of this class are a three-fold axis normal to a plane

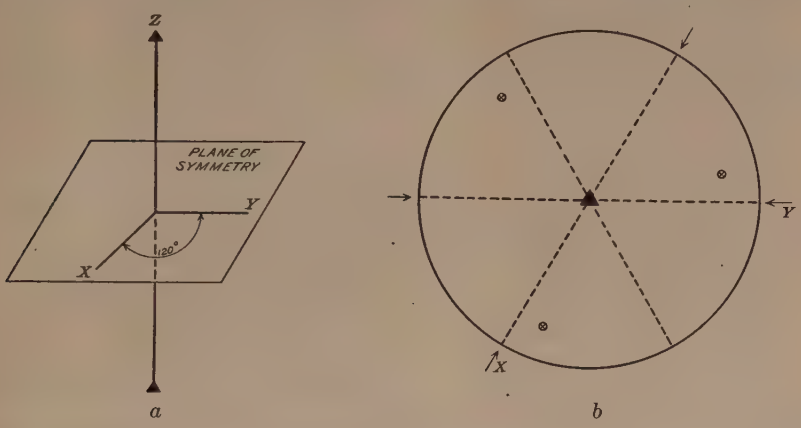


FIG. 38*a*.—The three-fold rotation axis and perpendicular plane of symmetry characteristic of the point group 6c.

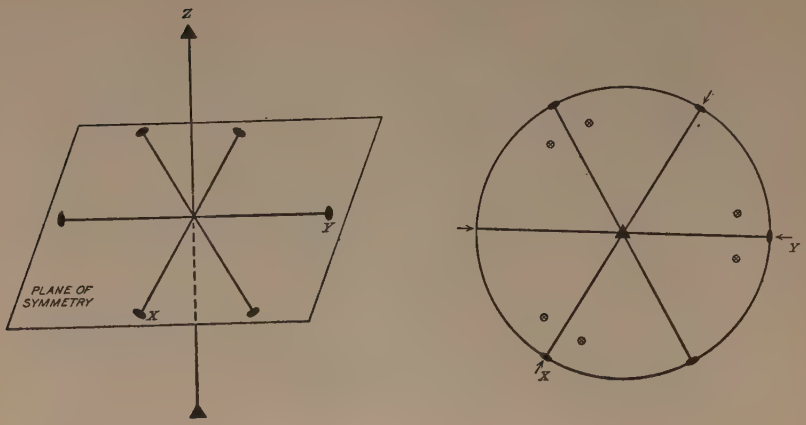
FIG. 38*b*.—The stereographic projection of the point group 6c.

of symmetry (Figure 38). Coördinates of equivalent points for hexagonal axes are:

$$xyz;\ y-x, \bar{x}, z;\ \bar{y}, x-y, z;\ xy\bar{z};\ y-x, \bar{x}, \bar{z};\ \bar{y}, x-y, \bar{z}.$$

Point group 6d, (D_{3^h}) [Trigonal holohedral class]. The elements of symmetry are those of 3D and a plane of symmetry coincident with that of the two-fold axes (Figure 39, *a* and *b*). As the projection of Figure 39 *b* shows, these elements give rise also to three auxiliary vertical planes of symmetry each of which contains the trigonal axis and one of the digonal axes. The coördinates of equivalent points are those of 3D and

$$xy\bar{z};\ y-x, \bar{x}, \bar{z};\ \bar{y}, x-y, \bar{z};\ x-y, \bar{y}, z;\ yxz;\ \bar{x}, y-x, z.$$



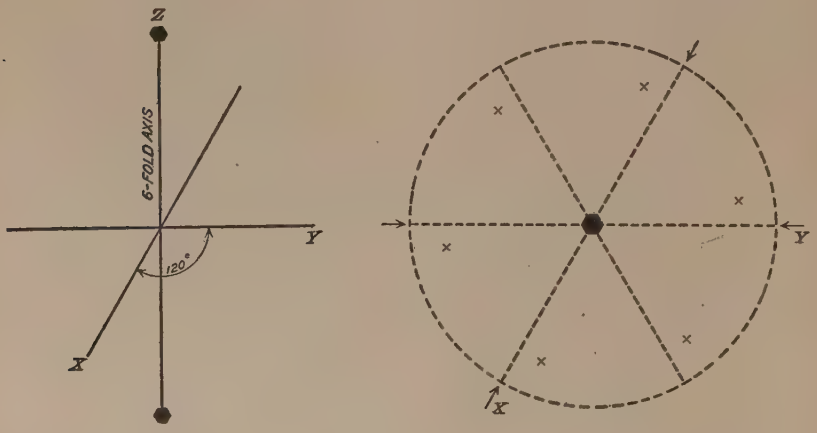
a *b*

FIG. 39*a*.—Symmetry properties of the point group 6d. The vertical diagonal planes of symmetry which also are present have not been shown.

FIG. 39*b*.—The stereographic projection of the point group 6d.

Point group 6C, (C_6) [Tetartohedral class]. This group consists of a single six-fold axis of symmetry (Figure 40, *a* and *b*). The coördinates of equivalent points are:

$$xyz;\ y, y - x, z;\ y - x, \bar{x}, z;\ \bar{x}\bar{y}z;\ \bar{y}, x - y, z;\ x - y, x, z.$$



a *b*

FIG. 40*a*.—The single six-fold axis of the point group 6C.

FIG. 40*b*.—The stereographic projection of the point group 6C.

Point group 6Ci, (C_6^h) [Paramorphic hemihedral class]. The positions of the plane of symmetry and the six-fold axis normal to it are shown in Figure 41, *a* and *b*. Since the operations of a six-fold rotation axis con-

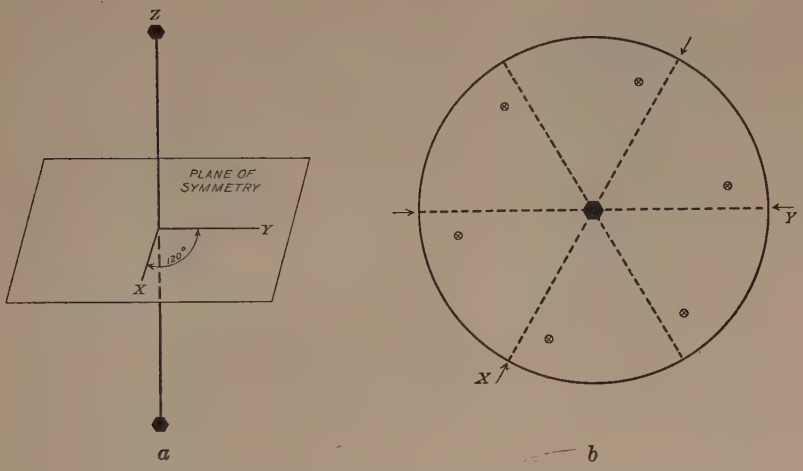


Fig. 41*a*.—The symmetry properties of the point group 6Ci.
Fig. 41*b*.—The stereographic projection of the point group 6Ci.

tain those of a two-fold axis, the elements of this group make the origin a center of symmetry. Coördinate positions of this group are those of 6C and:

$$xy\bar{z};\ y, y-x, \bar{z};\ y-x, \bar{x}, \bar{z};\ \bar{x}\bar{y}\bar{z};\ \bar{y}, x-y, \bar{z};\ x-y, x, \bar{z}.$$

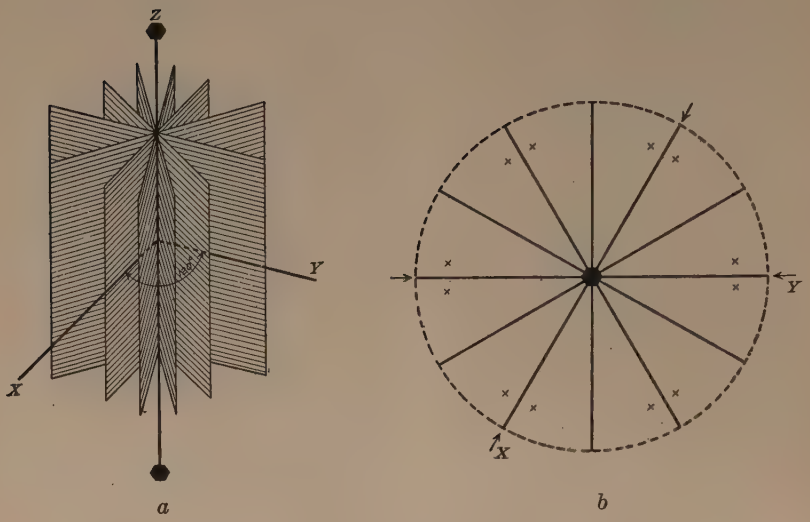
Point group 6e, (C_6^v) [Hemimorphic hemihedral class]. The arrangement of the six-fold axis and the reflecting planes characteristic of this class is shown in Figure 42, *a* and *b*. The coördinates of the equivalent points are those of 6C and:

$$\bar{x}, y-x, z;\ y-x, y, z;\ yxz;\ x, x-y, z;\ x-y, \bar{y}, z;\ \bar{y}\bar{x}z.$$

Point group 6D, (D_6) [Enantiomorphic hemihedral class]. The arrangement of the six-fold principal axis and the six coplanar axes is shown in Figure 43, *a* and *b*. Coördinates of the equivalent points are those of 6C and:

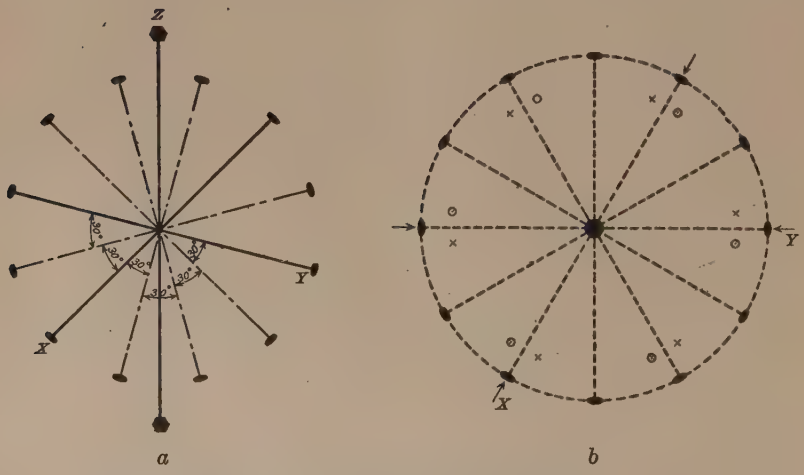
$$\bar{x}, y-x, \bar{z};\ y-x, y, \bar{z};\ yx\bar{z};\ x, x-y, \bar{z};\ x-y, \bar{y}, \bar{z};\ \bar{y}\bar{x}\bar{z}.$$

Point group 6Di, (D_6^h) [Holohedral class]. The elements of symmetry are those of 6D and a plane of symmetry coincident with that of the two-fold axes. As with 6Ci this combination of symmetry elements makes



a *b*

FIG. 42*a*.—The symmetry properties of the point group 6e.
FIG. 42*b*.—The stereographic projection of the point group 6e.



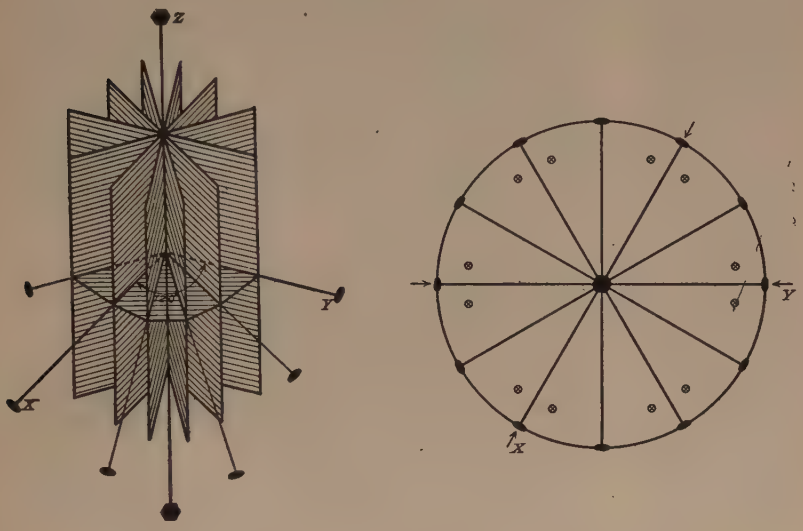
a *b*

FIG. 43*a*.—The symmetry axes of the point group 6D.
FIG. 43*b*.—The stereographic projection of the point group 6D.

the origin a center of symmetry (Figure 44, *a* and *b*). The coördinates of equivalent points are consequently those of 6D and:

$\bar{x}\bar{y}\bar{z}$; $\bar{y}, x-y, \bar{z}$; $x-y, x, \bar{z}$; $xy\bar{z}$; $y, y-x, \bar{z}$; $y-x, \bar{x}, \bar{z}$;

$x, x-y, z$; $x-y, \bar{y}, z$; $\bar{y}\bar{x}z$; $\bar{x}, y-x, z$; $y-x, y, z$; yxz.



a *b*

FIG. 44*a*.—The symmetry properties of the point group 6Di.
FIG. 44*b*.—The stereographic projection of the point group 6Di.

Numerous systems of naming the point groups have been proposed and are in more or less common use. A comparison of nomenclatures for some of those most frequently met is given in Table I.

Indices of Crystal Planes and Faces.—For the purpose of describing the positions of the faces and the intimate characteristics of a crystal a means of accurately defining a plane is necessary. It is customary to designate a crystal plane by three numbers, its Miller indices. These indices are obtained by taking the numerators of the reciprocals of the intercepts (chosen as multiples of the unit axial lengths) on the three coördinate axes of reference when these reciprocals have been reduced to a lowest common denominator. The systems of coördinate axes used are those which have been defined for the systems of symmetry. Except in cubic crystals the ratio of the unit lengths of these axes, the angles between the axes, or both, will be different for different crystals. This ratio between the unit lengths of the axes (usually written $a : b : c = ? : 1 : ?$) is called the *axial ratio;* the *axial angles* (α, β, γ) are the angles

TABLE I.

Symbol 1	Symbol 2	Class of Symmetry Schoenflies	Class of Symmetry Dana	Groth	No. of Symmetry Operations and Equivalent Points
I. Triclinic System					
C_1	1C	Hemihedry	Asymmetric	Asymmetric pedial	1
C_i	1Ci	Holohedry	Normal	Pinacoidal	2
II. Monoclinic System					
C_s	2c	Hemihedry	Clinohedral	Domatic	2
C_2	2C	Hemimorphic hemihedry	Hemimorphic	Monoclinic sphenoidal	2
C_2^h	2Ci	Holohedry	Normal	Monoclinic prismatic	4
III. Orthorhombic System					
C_2^v	2e	Hemimorphic hemihedry	Hemimorphic	Rhombic pyramidal	4
V	2D	Enantiomorphic hemihedry	Sphenoidal	Rhombic bisphenoidal	4
V^h	2Di	Holohedry	Normal	Rhombic bipyramidal	8
IV. Tetragonal System					
S_4	4c	Tetartohedry of the second sort	Tetartohedral	Tetragonal bisphenoidal	4
V^d	4d	Hemihedry of the second sort	Sphenoidal	Tetragonal scalenohedral	8
C_4	4C	Tetartohedry	Pyramidal hemimorphic	Tetragonal pyramidal	4
C_4^h	4Ci	Paramorphic hemihedry	Pyramidal	Tetragonal bipyramidal	8
C_4^v	4e	Hemimorphic hemihedry	Hemimorphic	Ditetragonal pyramidal	8
D_4	4D	Enantiomorphic hemihedry	Trapezohedral	Tetragonal trapezohedral	8
D_4^h	4Di	Holohedry	Normal	Ditetragonal bipyramidal	16
V. Cubic System					
T	T	Tetartohedry	Tetartohedral	Tetrahedral pentagonal dodecahedral	12
T^h	Ti	Paramorphic hemihedry	Pyritohedral	Diacisdodecahedral	24
T^d	Te	Hemimorphic hemihedry	Tetrahedral	Hexacistetrahedral	24
O	O	Enantiomorphic hemihedry	Plagihedral	Pentagonalicositetrahedral	24
O^h	Oi	Holohedry	Normal	Hexacisoctahedral	48

VI. Hexagonal System

			Rhombohedral Division		
C_3	3C	Tetartohedry	24.	Trigonal pyramidal	3
C_3^i	3Ci	Hexagonal tetartohedry of the second sort	Trirhombohedral	Rhombohedral	6
C_3^v	3e	Hemimorphic hemihedry	Ditrigonal pyramidal	Ditrigonal pyramidal	6
D_3	3D	Enantiomorphic hemihedry	Trapezohedral	Trigonal trapezohedral	6
D_3^d	3Di	Holohedry	Rhombohedral	Ditrigonal scalenohedral	12
			Hexagonal Division		
C_3^h	6c	Trigonal paramorphic hemihedry	23.	Trigonal bipyramidal	6
D_3^h	6d	Trigonal holohedry	Trigonotype	Ditrigonal bipyramidal	12
C_6	6C	Tetartohedry	Pyramidal hemimorphic	Hexagonal pyramidal	6
C_6^h	6Ci	Paramorphic hemihedry	Pyramidal	Hexagonal bipyramidal	12
C_6^v	6e	Hemimorphic hemihedry	Hemimorphic	Dihexagonal pyramidal	12
D_6	6D	Enantiomorphic hemihedry	Trapezohedral	Hexagonal trapezohedral	12
D_6^h	6Di	Holohedry	Normal	Dihexagonal bipyramidal	24

NOTE: The symbols under column (1) are the original ones of A. Schoenflies (Krystallsysteme u. Krystallstruktur (Leipzig, 1891); those in column (2) are the modified Hilton symbols (R. W. G. Wyckoff, Am. J. Sci. *6*, 288 (1923)) which are used throughout this book.

between these axes. In Figure 45 a, b and c are unit lengths along the axes X, Y and Z; $\angle\alpha$, $\angle\beta$ and $\angle\gamma$ are the angles between YZ, XZ and XY respectively. The intercepts of the plane MNP on these axes are seen to be 2a, b and $\frac{1}{2}$c. The reciprocals of the coefficients of these unit axial lengths [$\frac{1}{2}$, 1, 2] yield the Miller indices (124). In describing planes in terms of the hexagonal axes four indices (hkil) are sometimes employed.

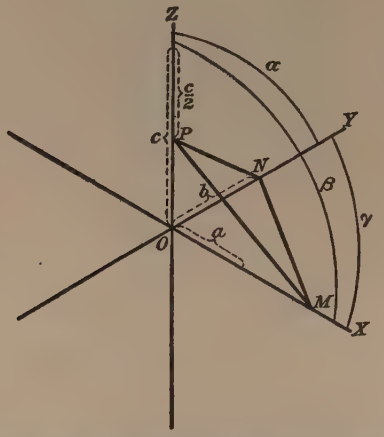


FIG. 45.—The intercepts of the plane MNP on the three coördinate axes X, Y and Z are 2a, b and $\frac{1}{2}$c; its Miller indices consequently are (124).

The additional index is derived from the intercepts of the plane upon a third coördinate axis lying in the plane of X and Y (Figure 46) and making an angle of 120° with the latter. It can be shown that with axes of this sort h + k is equal to $\bar{\text{i}}$, if i is the index of the new axis; that is h + k + i = 0. For the description of the faces occurring upon a crystal this additional axis is of value but for other purposes it may profitably be omitted.

The form of the equation for a plane with the Miller indices (hkl) referred to cubic axes is readily obtained. The intercepts of the plane MNP of Figure 45 along the coördinate axes X, Y and Z are OM, ON and OP. In its intercept form the equation of this plane is $x'/OM + y'/ON + z'/OP = 1$. Since the unit length along each of these cubic axes is the same, OM, ON, and OP can be written as ma_0, na_0 and pa_0, where a_0 is this unit length. Then

$$x'/ma_0 + y'/na_0 + z'/pa_0 = 1, \text{ or } npx' + mpy' + mnz' = mnpa_0.$$

Since m, n and p are the intercept multiples of a_0 along the axes, the Miller indices (hkl) of MNP are by definition the numerators of their reciprocals [1/m, 1/n, 1/p] put over a common denominator — np/mnp,

mp/mnp, mn/mnp — and divided by their greatest common divisor (r). Thus rh = np, rk = mp and rl = mn. This yields

$$hx' + ky' + lz' = a_0mnp/r, \quad \text{or}$$
$$hx' + ky' + lz' - D = 0, \quad \text{where } D = a_0mnp/r \ldots\ldots (1)$$

A plane parallel to $Ax' + By' + Cz' - D = 0$ and passing through the point $P(x_1'y_1'z_1')$ is

$$Ax' + By' + Cz' - (Ax_1' + By_1' + Cz_1') = 0.$$

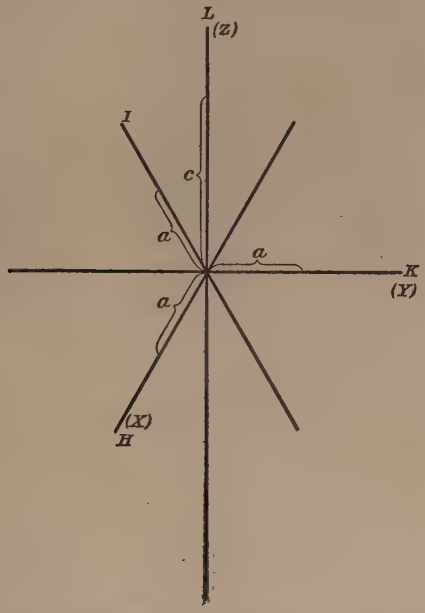


FIG 46.—The hexagonal axes of reference. The I axis, in the plane of H and K, makes an angle of 120° with them.

Consequently one having the indices (hkl) and containing the origin will be expressed by

$$hx' + ky' + lz' = 0 \ldots\ldots\ldots\ldots\ldots\ldots (1a)$$

The equation of (hkl) referred to the coördinate axes of systems of less symmetry will be similar in form, the added complexities being of a purely analytical nature. Thus, for instance, in orthorhombic axes (hkl) is defined by the equation

$$x'h/a + y'k + z'l/c - D = 0, \text{ where } a : 1 : c \text{ is the axial ratio.}$$

The Law of Rational Indices.—It is observed that all of the faces occurring upon any crystal can be described by indices which are integers; furthermore these integers are usually small numbers. This rule, which in its essence is purely an experimental one is known as the *law of rational indices*. The assumption of its universal applicability is fundamental to all of the developments of mathematical crystallography.

Zones.—The equations (referred to cubic axes) of two planes parallel to two crystal faces having the indices (hkl) and (h'k'l') and passing through the origin have been seen to be [1]

$$hx' + ky' + lz' = 0 \quad \text{and}$$
$$h'x' + k'y' + l'z' = 0.$$

The equation of the line of intersection of these two planes, which will contain the origin and be parallel to an edge of the crystal, can be written

$$\frac{x}{kl' - lk'} = \frac{y}{lh' - hl'} = \frac{z}{hk' - kh'}.$$

All of the planes (or crystal faces) parallel to this line lie in a *zone*, of which it is the *zone axis*. The three numbers $u = kl' - lk'$, $v = lh' - hl'$ and $w = hk' - kh'$ (usually written [uvw]) are the *indices of the zone*. Just as two non-parallel planes determine a zone axis, so two intersecting zone axes determine a possible crystal face. The indices of such a plane are expressed by the analogous relation: $h = vw' - wv'$, $k = wu' - uw'$, $l = uv' - vu'$. These two expressions are frequently employed in the determination of the indices of faces and planes in crystals. Since the indices of a plane are always integers, it is evident that the indices of a zone must likewise be whole numbers.

Forms.—For any crystal face (hkl), there will be other geometrically identical faces; in number they will either equal or be an integral submultiple of operations of the symmetry elements possessed by the crystal. These equivalent planes together constitute the faces of a *form*. For many purposes it is necessary to know the indices of different planes belonging to a specified form. They can be obtained through the coördinates of equivalent points of the crystal classes, since each of these sets of coördinates will yield the intercepts of a plane of the form (hkl). Thus the indices of the planes of the most general form having the symmetry of the point group 4C may be found in the following manner. The three intercepts of the plane (hkl) are:

$$x00;\ 0y0;\ 00z.$$

[1] These equations are readily generalized to apply in this same form to axial systems of less symmetry if $x' = ax$, $y' = y$ and $z' = cz$ are substituted in the corresponding equation

$$x'h/a + k'y + z'l/c = 0 \quad \text{to yield } hx + ky + lz = 0.$$

The operation which moves xyz to the position $\bar{y}xz$ will transfer these intercept points to

$$0x0;\ \bar{y}00;\ 00z.$$

With the aid of equation (1) the indices of the plane corresponding to these last three are found to be $(\bar{k}hl)$. Similarly the other two operations of the group give rise to the equivalent planes $(\bar{h}\bar{k}l)$ and $(k\bar{h}l)$. The application of this procedure to other point groups gives the indices of each of the planes of the most general forms (the forms in which h, k and l can have any integral values). If this is done it is seen that except for groups defined by hexagonal axes the indices of the faces of the most general form are the coördinates of the equivalent points of the group if x = h, y = k, z = l. For the hexagonal classes this simple relation does not hold unless Fedorov instead of cartesian coördinates are employed. The Fedorov coördinates [1] of a point are the distances along the coördinate axes from the origin to perpendiculars dropped from the point to these axes. The indices of planes in the general forms of point groups defined through the hexagonal axes of reference are contained in Table II.

TABLE II. INDICES OF GENERAL FORMS OF HEXAGONAL POINT GROUPS

(*a*) $hk\bar{i}l$; $ihkl$; $kihl$;
(*b*) $ikh\bar{l}$; $khi\bar{l}$; $hik\bar{l}$;
(*c*) $hki\bar{l}$; $ihk\bar{l}$; $kih\bar{l}$;
(*d*) $i\bar{k}\bar{h}l$; $\bar{k}\bar{h}\bar{i}l$; $\bar{h}\bar{i}\bar{k}l$;
(*e*) $\bar{h}\bar{k}\bar{i}l$; $\bar{i}\bar{h}\bar{k}l$; $\bar{k}\bar{i}\bar{h}l$;
(*f*) $\bar{i}\bar{k}\bar{h}l$; $\bar{k}\bar{h}\bar{i}l$; $\bar{h}\bar{i}\bar{k}l$;
(*g*) $\bar{h}\bar{k}\bar{i}l$; $\bar{i}\bar{h}\bar{k}l$; $\bar{k}\bar{i}\bar{h}l$;
(*h*) $ikhl$; $khil$; $hikl$.

Point group 3C.	The indices of (*a*).
Point group 3Ci.	The indices of (*a*) and (*g*).
Point group 3e.	The indices of (*a*) and (*h*).
Point group 3D.	The indices of (*a*) and (*b*).
Point group 3Di.	The indices of (*a*), (*b*), (*g*) and (*d*).
Point group 6c.	The indices of (*a*) and (*c*).
Point group 6d.	The indices of (*a*), (*b*), (*c*) and (*h*).
Point group 6C.	The indices of (*a*) and (*e*).
Point group 6Ci.	The indices of (*a*), (*e*), (*c*) and (*g*).
Point group 6e.	The indices of (*a*), (*e*), (*d*) and (*h*).
Point group 6D.	The indices of (*a*), (*e*), (*b*), and (*f*).
Point group 6Di.	The indices of (*a*), (*b*), (*c*), (*d*), (*e*), (*f*), (*g*) and (*h*).

A form with faces perpendicular to axes of symmetry will have fewer than the number of faces in the general form of its symmetry class. Since these special forms thus arise from the coincidence of two or more of the planes of the general form, they can all be found by equating in turn the indices of every other plane of the general form to the first one (hkl). For

[1] H. Hilton, Mathematical Crystallography (Oxford, 1904), p. 74.

example the indices of the general form for the point group 2Di (the holohedry of the orthorhombic system) are (page 28):

$$(hkl);\ (h\bar{k}\bar{l});\ (\bar{h}k\bar{l});\ (\bar{h}\bar{k}l);\ (\bar{h}\bar{k}\bar{l});\ (\bar{h}kl);\ (h\bar{k}l);\ (hk\bar{l});$$

The indices $(h\bar{k}\bar{l}) = (hkl)$ when $k = l = 0$. Consequently the operation of symmetry which makes the plane (hkl) coincide with $(h\bar{k}\bar{l})$ will leave the plane (100) unchanged. By substituting these values of h, k and l in the indices of the other planes it appears that (100) and $(\bar{1}00)$ together constitute a special form of this point group. In the same way equating (hkl) to $(\bar{h}k\bar{l})$, $(\bar{h}kl)$, etc. leads to the form (010); $(0\bar{1}0)$, to the form (0kl); $(0k\bar{l})$; $(0k\bar{l})$; $(0\bar{k}l)$, etc. The continued application of this procedure furnishes the following special forms of each of the point groups (Table III). As already stated the indices of the general forms can be

TABLE III. THE SPECIAL FORMS OF THE POINT GROUPS

I. Triclinic System.
1. 1C No special forms.
2. 1Ci No special forms.

II. Monoclinic System.
3. 2c (*a*) hk0.
4. 2C (*a*) 001. (*b*) 00$\bar{1}$.
5. 2Ci (*a*) 001; 00$\bar{1}$. (*b*) hk0; $\bar{h}\bar{k}$0.

III. Orthorhombic System.
6. 2e (*a*) 001. (*b*) 00$\bar{1}$. (*c*) 0kl; 0$\bar{k}$l. (*d*) h0l; $\bar{h}$0l.
7. 2D (*a*) 100; $\bar{1}$00. (*b*) 010; 0$\bar{1}$0. (*c*) 001; 00$\bar{1}$.
8. 2Di (*a*) 100; $\bar{1}$00. (*b*) 010; 0$\bar{1}$0. (*c*) 001; 00$\bar{1}$. (*d*) 0kl; 0$\bar{k}\bar{l}$; 0k$\bar{l}$; 0$\bar{k}$l. (*e*) h0l; h0$\bar{l}$; $\bar{h}$0$\bar{l}$; $\bar{h}$0l. (*f*) hk0; h$\bar{k}$0; $\bar{h}$k0; $\bar{h}\bar{k}$0.

IV. Tetragonal System.
9. 4c (*a*) 001; 00$\bar{1}$.
10. 4C (*a*) 001. (*b*) 00$\bar{1}$.
11. 4d (*a*) 100; $\bar{1}$00. (*b*) 010; 0$\bar{1}$0. (*c*) 001; 00$\bar{1}$. (*d*) hhl; h$\bar{h}\bar{l}$; $\bar{h}$h$\bar{l}$; $\bar{h}\bar{h}$l.
12. 4Ci (*a*) 001; 00$\bar{1}$. (*b*) hk0; $\bar{k}$h0; $\bar{h}\bar{k}$0; k$\bar{h}$0.
13. 4e (*a*) 001. (*b*) 00$\bar{1}$. (*c*) 0kl; $\bar{k}$0l; 0$\bar{k}$l; k0l. (*d*) hhl; $\bar{h}$hl; $\bar{h}\bar{h}$l; h$\bar{h}$l.
14. 4D (*a*) 001; 00$\bar{1}$. (*b*) 100; 010; $\bar{1}$00; 0$\bar{1}$0. (*c*) 1$\bar{1}$0; 110; $\bar{1}$10; $\bar{1}\bar{1}$0.
15. 4Di (*a*) 001; 00$\bar{1}$. (*b*) 100; 010; $\bar{1}$00; 0$\bar{1}$0. (*c*) 1$\bar{1}$0; 110; $\bar{1}$10; $\bar{1}\bar{1}$0. (*d*) hk0; $\bar{k}$h0; k$\bar{h}$0; h$\bar{k}$0; $\bar{h}\bar{k}$0; $\bar{h}$k0; kh0; $\bar{h}\bar{k}$0. (*e*) 0kl; $\bar{k}$0l; 0$\bar{k}$l; k0l; 0$\bar{k}\bar{l}$; $\bar{k}$0$\bar{l}$; 0k$\bar{l}$; k0$\bar{l}$. (*f*) hhl; $\bar{h}$hl; $\bar{h}\bar{h}$l; h$\bar{h}$l; $\bar{h}$h$\bar{l}$; h$\bar{h}\bar{l}$; $\bar{h}$h$\bar{l}$; hh$\bar{l}$.

V. Cubic System.
16. T (*a*) 111; 1$\bar{1}\bar{1}$; $\bar{1}$1$\bar{1}$; $\bar{1}\bar{1}$1. (*b*) $\bar{1}\bar{1}\bar{1}$; $\bar{1}$11; 1$\bar{1}$1; 11$\bar{1}$. (*c*) 100; $\bar{1}$00; 010; 0$\bar{1}$0; 001; 00$\bar{1}$.
17. Ti (*a*) 100; $\bar{1}$00; 010; 0$\bar{1}$0; 001; 00$\bar{1}$. (*b*) 111; 1$\bar{1}\bar{1}$; $\bar{1}$1$\bar{1}$; $\bar{1}\bar{1}$1; $\bar{1}\bar{1}\bar{1}$; $\bar{1}$11; 1$\bar{1}$1; 11$\bar{1}$. (*c*) 0kl; 0$\bar{k}\bar{l}$; 0k$\bar{l}$; 0$\bar{k}$l; l0k; $\bar{l}$0$\bar{k}$; $\bar{l}$0k; k$\bar{l}$0; $\bar{k}\bar{l}$0; k$\bar{l}$0; $\bar{k}$l0.
18. Te (*a*) 111; 1$\bar{1}\bar{1}$; $\bar{1}$1$\bar{1}$; $\bar{1}\bar{1}$1. (*b*) $\bar{1}\bar{1}\bar{1}$; $\bar{1}$11; 1$\bar{1}$1; 11$\bar{1}$. (*c*) 100; $\bar{1}$00; 010; 0$\bar{1}$0; 001; 00$\bar{1}$. (*d*) hhl; h$\bar{h}\bar{l}$; $\bar{h}$h$\bar{l}$; $\bar{h}\bar{h}$l; lhh; $\bar{l}$h$\bar{h}$; l$\bar{h}\bar{h}$; hlh; h$\bar{l}$h; $\bar{h}$l$\bar{h}$.
19. O (*a*) 100; $\bar{1}$00; 010; 0$\bar{1}$0; 001; 00$\bar{1}$. (*b*) 111; 1$\bar{1}\bar{1}$; $\bar{1}$1$\bar{1}$; $\bar{1}\bar{1}$1; $\bar{1}\bar{1}\bar{1}$; $\bar{1}$11; 1$\bar{1}$1; 11$\bar{1}$. (*c*) 1$\bar{1}$0; 110; $\bar{1}$10; $\bar{1}\bar{1}$0; 011; 01$\bar{1}$; 0$\bar{1}$1; 0$\bar{1}\bar{1}$; 101; $\bar{1}$01; 10$\bar{1}$; $\bar{1}$0$\bar{1}$.

20. Oi (*a*) 100; $\bar{1}00$; 010; $0\bar{1}0$; 001; $00\bar{1}$. (*b*) 111; $1\bar{1}\bar{1}$; $\bar{1}1\bar{1}$; $\bar{1}\bar{1}1$; $\bar{1}\bar{1}\bar{1}$; $\bar{1}11$; $1\bar{1}1$; $11\bar{1}$. (*c*) $1\bar{1}0$; 110; $\bar{1}10$; $\bar{1}\bar{1}0$; 011; $01\bar{1}$; $0\bar{1}1$; $0\bar{1}\bar{1}$; 101; $\bar{1}01$; $10\bar{1}$; $\bar{1}0\bar{1}$. (*d*) 0kl; $0k\bar{l}$; $0\bar{k}l$; $0\bar{k}\bar{l}$; h0k; $\bar{h}0k$; $h0\bar{k}$; $\bar{h}0\bar{k}$; kh0; $k\bar{h}0$; $\bar{k}h0$; $\bar{k}\bar{h}0$; k0l; $k0\bar{l}$; $\bar{k}0l$; $\bar{k}0\bar{l}$; 0lk; $0l\bar{k}$; $0\bar{l}k$; $0\bar{l}\bar{k}$; lk0; $l\bar{k}0$; $\bar{l}k0$; $\bar{l}\bar{k}0$. (*e*) hhl; $h\bar{h}l$; $\bar{h}hl$; $\bar{h}\bar{h}l$; lhh; $l\bar{h}h$; $\bar{l}\bar{h}h$; $l\bar{h}\bar{h}$; hlh; $h\bar{l}h$; $\bar{h}lh$; $\bar{h}\bar{l}h$; $\bar{h}h\bar{l}$; $\bar{h}hl$; hhl; $l\bar{h}\bar{h}$; $l\bar{h}h$; $lh\bar{h}$; $\bar{l}hh$; $h\bar{l}\bar{h}$; $h\bar{l}h$; $\bar{h}lh$; $h\bar{l}\bar{h}$.

VI. Hexagonal System.

A. Rhombohedral Division

21. 3C Rhombohedral Axes: (*a*) 111; (*b*) $\bar{1}\bar{1}\bar{1}$. Hexagonal Axes: (*a'*) 0001. (*b'*) $000\bar{1}$.
22. 3Ci Rhombohedral Axes: (*a*) 111; $\bar{1}\bar{1}\bar{1}$. Hexagonal Axes: (*a'*) 0001; $000\bar{1}$.
23. 3e Rhombohedral Axes: (*a*) 111. (*b*) $\bar{1}\bar{1}\bar{1}$. (*c*) hhl; lhh; hlh. Hexagonal Axes: (*a'*) 0001. (*b'*) $000\bar{1}$. (*c'*) h, h, $2\bar{h}$, l; $2\bar{h}$, h, h, l; h, $2\bar{h}$, h, l.
24. 3D Rhombohedral Axes: (*a*) 111; $\bar{1}\bar{1}\bar{1}$. (*b*) $1\bar{1}0$; $01\bar{1}$; $\bar{1}01$. (*c*) $\bar{1}10$; $0\bar{1}1$; $10\bar{1}$. Hexagonal Axes: (*a'*) 0001; $000\bar{1}$. (*b'*) $11\bar{2}0$; $\bar{2}110$; $1\bar{2}10$. (*c'*) $\bar{1}\bar{1}20$; $2\bar{1}\bar{1}0$; $\bar{1}2\bar{1}0$.
25. 3Di Rhombohedral Axes: (*a*) 111; $\bar{1}\bar{1}\bar{1}$. (*b*) $1\bar{1}0$; $01\bar{1}$; $\bar{1}01$; $\bar{1}10$; $0\bar{1}1$; $10\bar{1}$. (*c*) hhl; lhh; hlh; $\bar{h}h\bar{l}$; $l\bar{h}\bar{h}$; $\bar{h}l\bar{h}$. Hexagonal Axes: (*a'*) 0001; $000\bar{1}$. (*b'*) $11\bar{2}0$; $\bar{2}110$; $1\bar{2}10$; $\bar{1}\bar{1}20$; $2\bar{1}\bar{1}0$; $\bar{1}2\bar{1}0$. (*c'*) $h\bar{h}0l$; $0h\bar{h}l$; $\bar{h}0hl$; $0\bar{h}hl$; $\bar{h}h0l$; $h0\bar{h}l$.

B. Hexagonal Division

26. 6c (*a*) 0001; $000\bar{1}$. (*b*) h, k, − (h + k), 0; − (h + k), h, k, 0; k, − (h + k), h, 0.
27. 6d (*a*) 0001; $000\bar{1}$. (*b*) $11\bar{2}0$; $\bar{2}110$; $1\bar{2}10$. (*c*) $\bar{1}\bar{1}20$; $2\bar{1}\bar{1}0$; $\bar{1}2\bar{1}0$. (*d*) h, h, $2\bar{h}$, l; $2\bar{h}$, h, h, l; h, $2\bar{h}$, h, l; $2\bar{h}$, h, h, $\bar{l}$; h, h, $2\bar{h}$, $\bar{l}$; h, $2\bar{h}$, h, $\bar{l}$. (*e*) h, k, − (h + k), 0; − (h + k), h, k, 0; k, − (h + k), h, 0; − (h + k), k, h, 0; k, h, − (h + k), 0; h, − (h + k), k, 0.
28. 6C (*a*) 0001. (*b*) $000\bar{1}$.
29. 6Ci (*a*) 0001; $000\bar{1}$. (*b*) h, k, − (h + k), 0; − (h + k), h, k, 0; k, − (h + k), − h, 0; − h, − k, (h + k), 0; (h + k), − h, − k, 0; − k, (h + k), − h, 0.
30. 6e (*a*) 0001. (*b*) $000\bar{1}$. (*c*) h, h, $2\bar{h}$, l; $2\bar{h}$, h, h, l; h, $2\bar{h}$, h, l; $\bar{h}$, $\bar{h}$, 2h, l; 2h, $\bar{h}$, $\bar{h}$, l; $\bar{h}$, 2h, $\bar{h}$, l. (*d*) $h\bar{h}0l$; $0h\bar{h}l$; $\bar{h}0hl$; $\bar{h}h0l$; $0\bar{h}hl$; $h0\bar{h}l$.
31. 6D (*a*) 0001; $000\bar{1}$. (*b*) $11\bar{2}0$; $\bar{2}110$; $1\bar{2}10$; $\bar{1}\bar{1}20$; $2\bar{1}\bar{1}0$; $\bar{1}2\bar{1}0$. (*c*) $1\bar{1}00$; $01\bar{1}0$; $\bar{1}010$; $\bar{1}100$; $0\bar{1}10$; $10\bar{1}0$.
32. 6Di (*a*) 0001; $000\bar{1}$. (*b*) $11\bar{2}0$; $\bar{2}110$; $1\bar{2}10$; $\bar{1}\bar{1}20$; $2\bar{1}\bar{1}0$; $\bar{1}2\bar{1}0$. (*c*) $1\bar{1}00$; $01\bar{1}0$; $\bar{1}010$; $\bar{1}100$; $0\bar{1}10$; $10\bar{1}0$. (*d*) h, k, − (h + k), 0; − (h + k), h, k, 0; k, − (h + k), h, 0; − h, − k, (h + k), 0; (h + k), − h, − k, 0; − k, (h + k), − h, 0; k, h, − (h + k), 0; − (h + k), k, h, 0; h, − (h + k), k, 0; − k, − h, (h + k), 0; (h + k), − k, − h, 0; − h, (h + k), − k, 0; (*e*) h, h, $2\bar{h}$, l; $2\bar{h}$, h, h, l; h, $2\bar{h}$, h, l; $\bar{h}$, $\bar{h}$, 2h, l; 2h, $\bar{h}$, $\bar{h}$, l; $\bar{h}$, 2h, $\bar{h}$, l; $2\bar{h}$, h, h, $\bar{l}$; h, h, $2\bar{h}$, $\bar{l}$; h, $2\bar{h}$, h, $\bar{l}$; 2h, $\bar{h}$, $\bar{h}$, $\bar{l}$; $\bar{h}$, $\bar{h}$, 2h, $\bar{l}$; $\bar{h}$, 2h, $\bar{h}$, $\bar{l}$. (*f*) $h\bar{h}0l$; $0h\bar{h}l$; $\bar{h}0hl$; $\bar{h}h0l$; $0\bar{h}hl$; $h0\bar{h}l$; $0h\bar{h}\bar{l}$; $h\bar{h}0\bar{l}$; $h0h\bar{l}$; $\bar{h}h0\bar{l}$; $h0\bar{h}\bar{l}$; $0\bar{h}h\bar{l}$.

obtained with the aid of Table II (for hexagonal crystals) and by substituting h, k and l for x, y and z in the description of equivalent points (for all other classes.)

It has usually been the practice in crystallographic description to choose the Y-axis as the principal axis for monoclinic and orthorhombic groups. In this work the Z-axis of coördinates will always be taken as

the principal axis.[1] Consequently if a monoclinic or orthorhombic crystal has been described by making the Y (or b) axis the principal one, it is necessary to interchange its Y and Z axes, and their indices, in order to obtain agreement with the method of description used here.

Miscellaneous.—It sometimes happens that crystals will develop which are built up of two or more individuals having a definite but not parallel arrangement. These are twins. Thus components of a twin may be turned through an angle of 180° about some line of the crystal (the twinning axis) or they may be reflections of one another in a plane (the twinning plane). The surface along which the two individuals are in contact is the composition plane. In some twins the components are entirely separate from one another except at the plane of meeting (the contact twins); in others the separate parts closely intergrow (the penetration twins). Though such compound crystals as these can frequently be distinguished, for instance by the presence of reentrant angles, many twinned forms imitate almost exactly a single crystal of a higher symmetry.

Symmetry characteristics have been obtained by other methods than the study of the distribution of like faces upon a single crystal. Of these the most widely usable as far as it goes, and perhaps the most reliable of all methods of studying symmetry, is an investigation of the optical properties. Attempts also are made to deduce symmetry from the shapes and arrangements of the tiny pits that result from a slight corrosion of crystal faces (the etch figures) or from the shapes of the bodies obtained by slowly dissolving single crystals (solution figures). Furthermore, when some crystals having a comparatively low degree of symmetry are heated or otherwise mechanically strained they develop regions of positive and negative electrification in the same specimen. Knowledge of symmetry properties can be obtained from a study of the distribution of these areas. Strongly magnetic crystals with low symmetry often have very different magnetic properties in different directions; their investigation would consequently give valuable information concerning symmetry.

The Internal Symmetry of Crystals

Discussion thus far has been concerned with the kinds of symmetry exhibited by a crystal as a whole. If several specimens of the same crystal are examined they are always found to exhibit the same symmetry characteristics no matter what may be their absolute size. Likewise if a large

[1] This is usually done in theoretical crystallography because of the greater logical consistency which results.

[2] Some of the space groups were deduced by L. Sohncke, Entwickelung einer Theorie der Krystallstruktur (Leipzig, 1879). All of the 230 space groups were deduced in three separate ways by:

rhombohedral fragment of calcite ($CaCO_3$), for example, is split into bits by successive blows it will *cleave* into many minute rhombohedrons each of which possesses the same symmetry properties as the original piece. Such observations as these early led to the conception of the problem of determining the manner in which the elements of symmetry are repeated and distributed throughout the body of a crystal.

The 32 point groups themselves give all of the ways in which elements of symmetry can be arranged about a single point in space to yield crystallographic symmetry. The problem, then, of the spacial grouping of symmetry elements in crystals is concerned with (1) the nature of the patterns according to which these point groups (or their equivalents) can be symmetrically distributed throughout space and (2) the investigation of other groups of points than the point groups which, when repeated according to these same *patterns*, will yield an aggregate having the necessary symmetry characteristics. The symmetrical patterns according to which these groups of points may be repeated are the *space lattices*; one of the spacial distributions of symmetry elements which as a whole has crystal symmetry is a *space group*. All of such indefinitely extended arrangements of elements with crystallographic symmetry appear to have been obtained through the development of the theory of space groups.

It can be shown that there is but one space lattice for triclinic crystals. Designated as Γ_{tr}, it is illustrated in Figure 47. The lines X, Y and Z are the triclinic axes of reference. The elements of symmetry associated with one point in space, such as O, must likewise be found about every other point of the lattice, A, B, C, . . . , etc. Distances between neighboring lattice points along the X-axis are all equal and are designated as $2\tau_x$, the *primitive translation* along this coördinate axis. Similarly the separations between neighboring points along the Y and the Z-axes are

(1) E. Fedorov, Zeitsch. f. Krystal. *24*, 209 (1895). This is an account of work published in Russian several years previously.

(2) A. Schoenflies, Krystallsysteme und Krystallstruktur (Leipzig, 1891)..

(3) W. Barlow, Zeitsch. f. Krystal. *23*, 1 (1894). A derivation of the space groups making use of methods of representation of both Fedorov and Schoenflies is to be found in

(4) H. Hilton, Mathematical Crystallography (Oxford, 1903). This work likewise contains a mathematical discussion of other phases of crystal symmetry. Space groups have also been reviewed by

(5) S. Kreutz, Elemente der Theorie der Krystallstruktur (Leipzig, 1915), who gives developments which have influenced the growth of European methods of crystal structure study. The most satisfactory discussion of the theory of space groups is to be found in a newly published book:

(6) A. Schoenflies, Theorie der Kristallstruktur (Berlin, 1923). The direct application of space group results in the determination of the structure of crystals using X-rays has been discussed by

(7) P. Niggli, Geometrische Krystallographie des Discontinuums (Leipzig, 1919) and by

(8) R. W. G. Wyckoff, Am. J. Sci. *1*, 124 (1921).

all equal to $2\tau_y$ and $2\tau_z$ respectively. The proportionality $a : b : c = 2\tau_x : 2\tau_y : 2\tau_z$, where $a : b : c$ is the axial ratio, must always hold true. A lattice thus may be defined, when necessary, by giving the nature of the coördinate axes, and the primitive translations along these axes, of points adjacent to one chosen as the origin. Accordingly the lattice

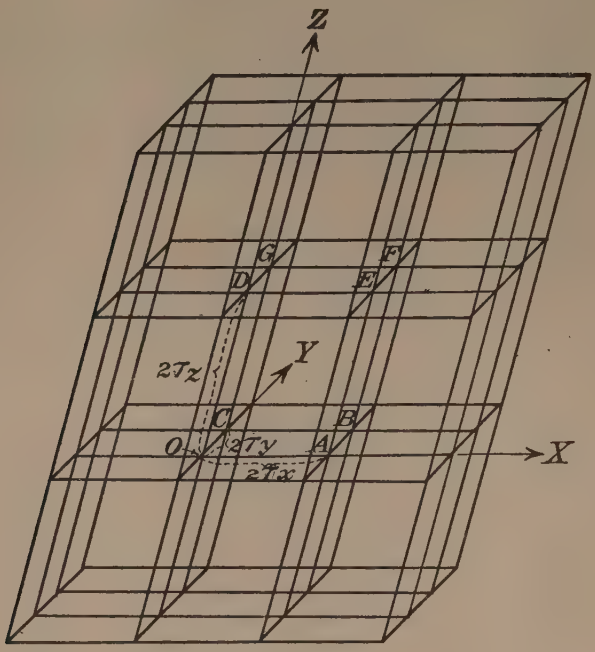


FIG. 47.—A portion from the triclinic space lattice Γ_{tr}. The prism OABCDEFG is the unit cell.

Γ_{tr} is completely described by giving its primitive translations along the triclinic axes as $\pm 2\tau_x$, $\pm 2\tau_y$, $\pm 2\tau_z$. In a similar fashion the primitive translations of the cubic space lattice Γ_c'' (Figure 48) are: $2\tau_x$; $2\tau_y$; $2\tau_z$; τ_x, τ_y, τ_z. There are 14 space lattices in all, identical with the 14 lattices of Bravais. Each has the complete symmetry of one of the seven systems of crystal symmetry. One is associated with triclinic, two with monoclinic, four with orthorhombic, two with tetragonal, three with cubic and two with hexagonal symmetry.

A space group, and in fact the only one, having hemihedral triclinic symmetry will be obtained by placing the point group 1C at each point of the space lattice Γ_{tr} (Figure 47). The group 1C has been said (page 23) to have only one-fold axes, the operations of which are simply to bring a

point into coincidence with itself. For any point x′y′z′, which for example may represent the center of an atom in a corresponding crystal, there will thus be other identically similar points, or atoms, only at $x' \pm 2\,m\tau_x$, $y' \pm 2\,n\tau_y$, $z' \pm 2\,p\tau_z$, where m, n and p can be any whole numbers including zero.

If the symmetry elements associated with 1Ci, on the other hand, are placed at the points of the same lattice, a space group isomorphous with the triclinic holohedry will result. 1Ci has a center of symmetry;

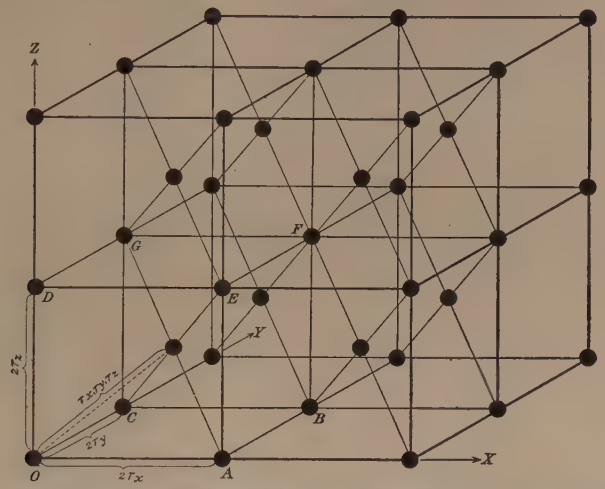


FIG. 48.—A portion from the "body centered" cubic space lattice Γ_c''. The cube OABCDEFG, with which are associated two points of the lattice, is the unit cell.

consequently (Figure 49) the space group [1] (1Ci — 1) consists of centers of symmetry located at the points of a triclinic lattice. With the origin at one of these centers the two points x′y′z′ and $\bar{x}'\bar{y}'\bar{z}'$ are equivalent to one another (as positions for identical atoms, etc.). All of such equivalent positions within the group will be given by the two sets of coördinates:

$$x' \pm 2\,m\tau_x,\ y' \pm 2\,n\tau_y,\ z' \pm 2\,p\tau_z;$$
$$-x' \pm 2\,m\tau_x,\ -y' \pm 2\,n\tau_y,\ -z' \pm 2\,p\tau_z$$

where, as before, m, n and p may be any integers including zero.

In order to discuss the properties of a space grouping of points it is convenient to select some portion the behavior of which will be representative of the indefinitely extended whole. For many purposes, including all those of crystal analysis, the *unit cell* may be taken as the

[1] The space group notation is a simple modification of that for the point groups: thus the space group 4Di-m (D_{4h}^{m}) is simply the mth space group to be defined which in its aggregate exhibits the symmetry of the point group 4Di (D_4^h).

smallest volume which will build up the entire grouping when repeated indefinitely by simple translations along the axes of coördinates. Reference to Figure 47 shows that the parallelopiped OABCDEFG is such an elementary prism for the space lattice Γ_{tr}. The similar unit prism for the

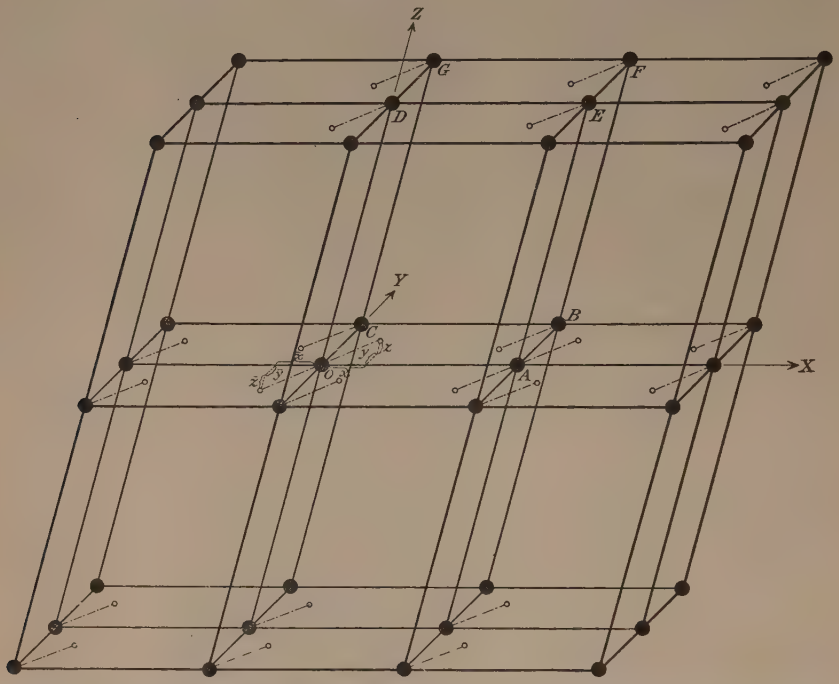


FIG. 49.—A portion from the space group (1Ci–1). Centers of symmetry, located at corners of the unit cells, are shown by black circles. The small open circles are equivalent points of the space group. The two points xyz and $\bar{x}\bar{y}\bar{z}$ are associated with the lattice point O.

space group (1Ci − 1) is shown in Figure 50. The two equivalent points contained within it are x′y′z′ and $2\tau_x - x'$, $2\tau_y - y'$, $2\tau_z - z'$. These coördinates become simpler by choosing as *unit domain* a region encircling the origin but still having the volume of the unit parallelopiped. The two equivalent points of (1C − 1) within this space are then: x′y′z′; $\bar{x}'\bar{y}'\bar{z}'$. These two representations are equivalent to one another in all essential respects. The unit cells of space groups with other symmetry have identically the same relation to the indefinitely extended grouping that the unit cell OABCDEFG (Figure 50) bears to the space group 1Ci − 1 of Figure 49. Thus if (Figure 47)

I. The side OA ≠ OC ≠ OD and the angle COA ≠ ∠DOA ≠ ∠DOC ≠ 90°, the unit is, as has just been stated, the triclinic unit cell.

If II. $OA \neq OC \neq OD$ and $\angle COA \neq 90°$ but $\angle DOA = \angle DOC = 90°$, the unit is monoclinic.

III. $OA \neq OC \neq OD$ and $\angle COA = \angle DOA = \angle DOC = 90°$ for the orthorhombic unit cell.

IV. $OA = OC \neq OD$ and $\angle COA = \angle DOA = \angle DOC = 90°$ for the tetragonal unit cell.

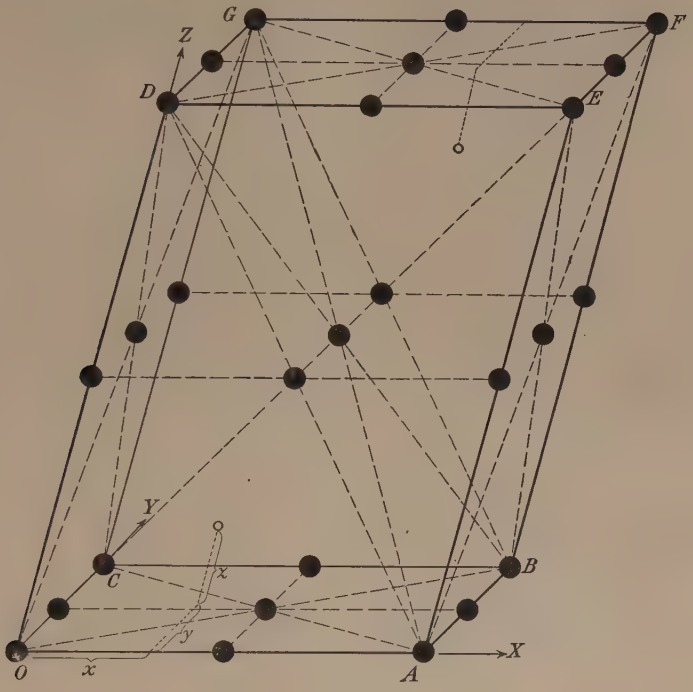


FIG. 50.—The unit cell of the space group 1Ci–1 giving all of its symmetry characteristics. Consideration shows that if centers of symmetry are located at O, A, B, etc., as in Fig. 49, there must also be centers at the other points marked by black circles in this figure. The two generally equivalent points contained within the unit are marked by open circles.

V. $OA = OC = OD$ and $\angle COA = \angle DOA = \angle DOC = 90°$ for the unit cube.

VI. $OA = OC = OD$ and $\angle COA = \angle DOA = \angle DOC \neq 90°$ for the unit rhombohedron.

VII. $OA = OC \neq OD$ and $\angle COA = 120°$ and $\angle DOA = \angle DOC = 90°$ for the hexagonal unit cell.

A geometrical account of a space group is supplied by the statement of the distribution of its symmetry elements about a point of its fundamental lattice together with the primitive translations of the latter. The coördinates of the equivalent points that are contained within the unit cell or the unit domain also supply all the information necessary for the reconstruction of a space group. Hence the preceding discussion has furnished a means of giving a simple and complete analytical description of a space group. For $1Ci - 1$ the equivalent positions within the triclinic unit have been shown to be $x'y'z'$ and $\bar{x}'\bar{y}'\bar{z}'$. An exactly similar representation can be given of all of the more complicated groups possessing higher symmetries.

It is more convenient for many purposes to use x, y and z as coördinates to represent fractional parts of the unit axial lengths (and of lengths of the sides of unit cells). These new coördinates then bear to x′, y′ and z′, which are absolute measures of distance, the relations $x = x'/a$, $y = y'/b$, $z = z'/c$ where a, b and c are the unit lengths along the X-, Y- and Z-axes of reference.

It has become customary to use coördinates of points within the unit domain because of their greater simplicity. Particularly on account of the easier representation by models, however, a space grouping is often described by giving the contents of the unit parallelopiped. This dual usage need introduce no difficulties if the practical identity of the two is borne in mind and if it is remembered that for every point of the unit domain having a negative component along one or more coördinate axes and thus lying outside the unit prism, coördinates of a corresponding point within the prism can be obtained by adding unit lengths along the appropriate axes. For example the coördinates of the equivalent points of the monoclinic space group $2Ci - 1$ are written:

$$xyz;\ \bar{x}\bar{y}z;\ \bar{x}\bar{y}\bar{z};\ xy\bar{z};\ \text{or}\ x'y'z';\ \bar{x}'\bar{y}'z';\ \bar{x}'\bar{y}'\bar{z}';\ x'y'\bar{z}'.$$

The complete coördinates of the equivalent points within the unit monoclinic prism then are

$$x'y'z';\ a - x', b - y', z';\ a - x', b - y', c - z';\ x', y', c - z.$$

The unit cell of this space group is shown in Figure 51. The coördinates of the equivalent points within the unit parallelopiped for each of the space groups can be obtained from those of the atoms in the unit domain in the same way.

It has already been suggested that the space groups define the positions that can be occupied by the atoms in crystals. Thus if an atom is located at the point xyz within a crystal, there must be exactly similar atoms at

each of the other equivalent points within the unit prism, or domain, of its corresponding space group and at the equivalent points arising from a repetition of this unit along the axes of reference. There may as a result

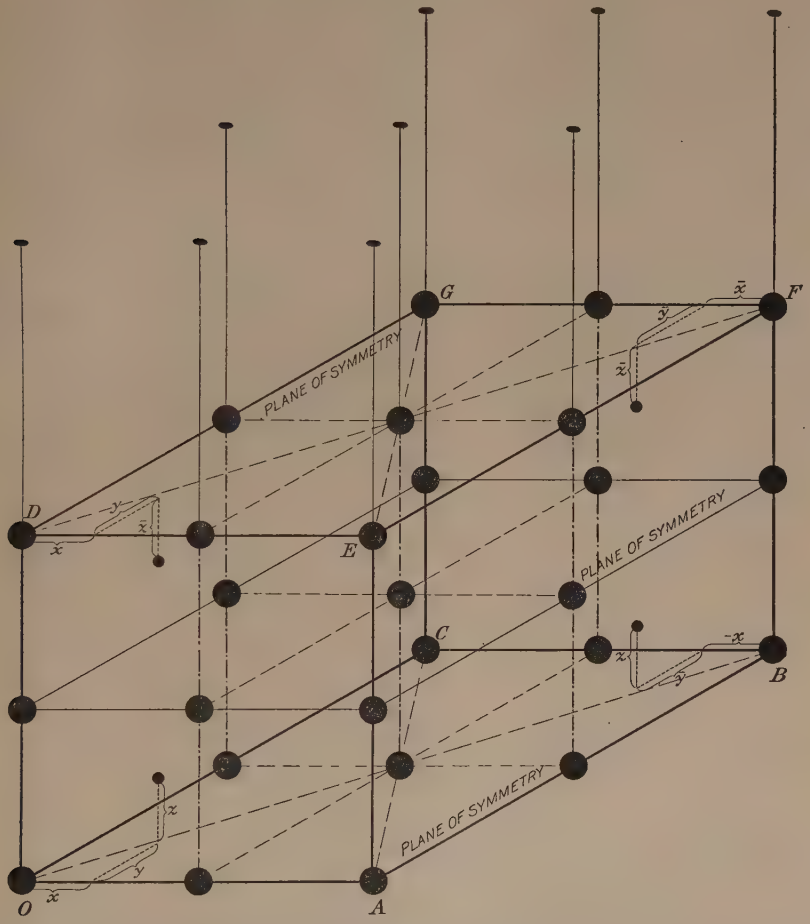


FIG. 51.—The unit cell of the monoclinic space group 2Ci−1. The two-fold axis DO perpendicular to the symmetry plane OABC makes the point O a center of symmetry. These elements of symmetry will be seen automatically to introduce the other elements shown in this figure. As before, large circles are centers of symmetry; the small circles show the four generally equivalent points contained within this unit

be as many atoms all alike within the unit prism of a crystal as there are equivalent points in the unit of its corresponding space group. This number will range anywhere from one, in the triclinic space group 1Ci − 1 just considered to 192 in such holohedral cubic groups as O − 5.

If, however, an equivalent point, or an atom, has such coördinates that it occupies a *special position* in lying in some element of symmetry, the number of the points like it will be less than the maximum number of *generally equivalent* points. For instance in the space group 1Ci − 1 (Figures 49 and 50), if x = y = z = 0, the two equivalent points xyz and $\bar{x}\bar{y}\bar{z}$ coalesce in the single special position 000 located at the origin, and other corners, of the unit prism.[1] Similarly by making x = y = z = $\frac{1}{2}$, or x = y = 0 and z = $\frac{1}{2}$, or x = y = $\frac{1}{2}$ and z = 0, the singly equivalent points $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$, $00\,\frac{1}{2}$, and $\frac{1}{2}\,\frac{1}{2}\,0$ will arise.[2] It is thus seen that the number is halved if an equivalent point lies in one of the centers of symmetry. The space group 4C − 1 will furnish another simple example. This group is obtained by placing the point group 4C at points of the first tetragonal space lattice Γ_t. This lattice differs from Γ_{tr} (Figure 47) in that its axes of reference are the mutually perpendicular tetragonal axes, two of which (X- and Y-) have equal unit lengths. Its primitive translations hence are $2\,\tau_x$, $2\,\tau_y$, $2\,\tau_z$ where $\tau_x = \tau_y$; and the unit cell is a right prism with a square base and points of the lattice at the corners. The coördinates of the generally equivalent points within the unit domain of 4C − 1 then are: xyz; $\bar{y}$xz; $\bar{x}\bar{y}$z; y$\bar{x}$z. Accordingly the equivalent positions (Figure 52) within this unit prism are x′y′z′; a − y′, x′, z′; a − x′, b − y′, z′; y′, b − x′, z′ where a = b in length. If an equivalent point lies in a four-fold axis, it will remain unaffected by the operations of this axis so that the four generally equivalent points will be reduced to single ones with either the coördinates (Figure 52) 00z or $\frac{1}{2}\frac{1}{2}$ z. The point $\bar{y}$xz arises from xyz by the operation of the 90° axis coincident with the Z-axis of reference; to find analytically the coördinates of the point which, lying in this rotation axis, will be unaffected by its operations, it is necessary to equate x, y and z to − y, x and z (or x′, y′ and z′ to a − y′, x′ and z′) respectively. This procedure leads directly to 00z and $\frac{1}{2}\frac{1}{2}$z, as before. All of these special cases of a space group can be obtained geometrically by placing a generally equivalent point successively upon each of the elements of symmetry which it possesses, or in a purely analytical way they can be found by continuing the procedure just outlined of equating the coördinates of every other equivalent point contained within the unit to the first point xyz.

Measurement of the X-ray diffraction effects from crystals seems to show conclusively that the number of chemical molecules associated with

[1] Though eight equivalent points, or atoms, in this special position are located at the eight corners of the unit parallelopiped only one complete point is associated with each unit. This may be imagined as due to the fact that with every one of these equivalent points contributing a part, and a different part, to eight different units, those at the corners of one unit parallelopiped together place a whole point within it.

[2] All of the other permutations of 0 and ½ taken three at a time also will furnish singly equivalent points of this group.

the unit cell is usually small. As positions for atoms these special positions thus become of the greatest importance and a knowledge of all of them is required for any serious application of space group theory to the determination of crystal structures. This information[1] has now been

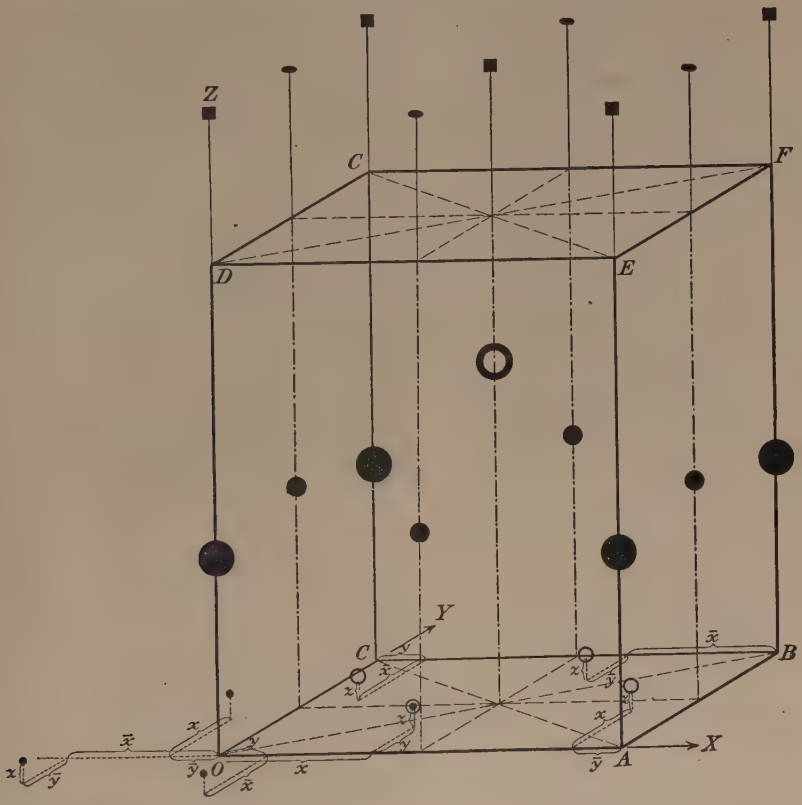


FIG. 52.—The unit cell of the tetragonal space group 4C−1. The single four-fold axis passing through the corner of the unit places another four-fold axis through the center and two-fold axes in the positions shown in this figure. The four equivalent points (marked by small black circles) grouped about the origin O may be taken as the points of the unit domain. The four generally equivalent points lying within the unit prism are marked by the small open circles. If the coördinates of these points are such that they lie upon the two-fold axes, their number is reduced to the two equivalent positions: $0\frac{1}{2}u$; $\frac{1}{2}0u$ (shown as medium sized black circles). Where the coördinate values are such as to place the equivalent points upon the four-fold axes, either the singly equivalent 00u (marked by large black circles) or the singly equivalent position $\frac{1}{2}\frac{1}{2}u$ (marked by a large annulus) is the result.

[1] The generally equivalent positions were stated in outline form by A. Schoenflies, Krystallsysteme und Krystallstruktur (Leipzig, 1891); some of the special cases are given in P. Niggli, Geometrische Krystallographie des Discontinuums (Leipzig, 1919); all are stated by R. W. G. Wyckoff, An Analytical Expression of the Results of the Theory of Space Groups (Carnegie Institution of Washington, Publication No. 318).

obtained and tabulated; numerous examples of its application will be give in subsequent chapters.

The character of this use can, however, be illustrated by a very simple case. If by some means it could be shown that the space group corresponding to a particular crystal of chemical composition RX_4 was $4C - 1$ and that one chemical molecule was associated with the unit, then the knowledge of the coördinates of all of the special and general cases of the space groups [1] shows that the atom R must have the position 00u (or $\frac{1}{2}\,\frac{1}{2}$ u) and the atoms of X the coördinates xyz; $\bar{y}xz$; $\bar{x}\bar{y}z$; $\bar{y}xz$; where of course u, x, y and z may have any fractional values. If the space group cannot be determined directly it still is possible to write down in this same way all of the atomic arrangements deducible from the several space groups having the type of symmetry exhibited by the crystal under examination.

It is believed that the theory of space groups gives a complete *geometrical* answer to the problem of the symmetry properties of crystals. As such it is a tool of the widest usefulness in the physical examination of crystals and their properties.

[1] R. W. G. Wyckoff, An Analytical Expression of the Results of the Theory of Space Groups (Washington, 1922), p. 79.

Chapter II. Some Properties of X-rays

X-radiation is produced whenever fast-moving electrons impinge upon matter. An X-ray tube is essentially a device for making possible this interaction. In its first forms it consisted of a glass tube with two metal electrodes between which a high voltage direct current could be passed. When the pressure in such a tube is reduced to a fraction of a millimeter electrons will be projected from the cathode and will give rise to X-rays on striking the metallic face of a target or anticathode interposed in their path. These early "gas tubes" are troublesome to operate because the character of the X-rays which they emit is conditioned in part by the pressure of the gas remaining in the tube and because this pressure itself changes as the tube is operated. X-ray tubes are now more often of the "hot cathode" (Coolidge or Lilienfeldt) type. In this form the bulb is evacuated as completely as possible, the flow of electrons being conditioned by the temperature of an electrically heated tungsten or alkaline earth covered wire acting as the cathode.

The nature of X-rays was in doubt for many years after their discovery. The observation of their diffraction by crystals and the successful interpretation of these effects in terms of the arrangements of the atoms in crystals has, however, shown unmistakably the fundamental similarity between X-rays and ordinary light radiations.

The Wave Length of X-rays.—From early attempts to obtain diffraction effects [1] with narrow slits, it was clear that if X-rays really were wave motions like light their lengths could not be greater than about 10^{-8} cm. The first determination [2] of the exact wave length of X-rays was furnished through their diffraction effects from crystals. This determination was not conclusive but the agreement of its results with the quantum conditions and the large mass of existing X-ray data permits no serious doubt of its correctness.

Studies of absorption of X-rays early indicated that the beam given out by an ordinary X-ray tube is not homogeneous. If, after the manner of Figure 53, a narrow pencil of X-rays defined by two lead slits strikes

[1] H. Haga u. C. H. Wind, Ann. d. Phys. *10*, 305 (1903); B. Walter u. R. Pohl, Ann. d. Phys. *25*, 715 (1908); 29, 331 (1908). A. Sommerfeld, Ibid. *38*, 473 (1912). P. P. Koch, Ibid. *38*, 507 (1912).

[2] W. H. Bragg, Proc. Roy. Soc. A. *89*, 246 (1913).

the face of a crystal C mounted upon the axis of a rotating table, the X-ray beam will be drawn out into a spectrum on a photographic plate at D. With X-rays analogous to light the following expression (Chapter III) connects the wave lengths λ with the atomic spacings of the "reflecting" crystal:[1]

$$n\lambda = 2\,d \sin\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where n is the "order" of the spectral reflection; λ is the wave length of the X-rays; d, the spacing between like atomic planes normal to the

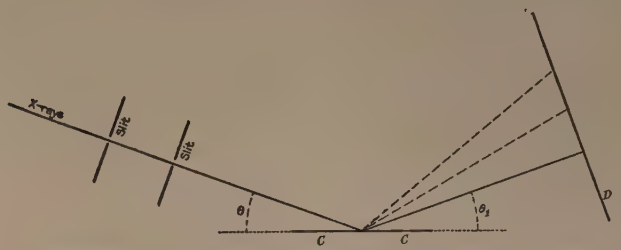


FIG. 53.—The arrangement for X-ray reflection. The beam of X-rays after passing through the slits strikes the crystal face C rotating about an axis normal to the plane of the paper and is spread out into a spectrum along D. When a ray is "reflected" from C the angle of incidence, θ, is equal to the angle of "reflection," θ_1.

reflecting crystal face, is a constant for the crystal used; and θ equals one half the angle of deviation of the X-ray beam. The spectrum thus obtained at about 50,000 volts from an X-ray tube having a tungsten target is shown in Figure 54; the cleavage (100) face of calcite is used as the crystal C (of Figure 53). This spectrum consists of two distinct parts: (1) sharp lines, the characteristic radiation, impressed upon (2) a more or less unbroken background. This background, composed of a continuous series of wave lengths, is commonly called the "white radiation" from its similarity to white light. Usually both types will be present in the radiation from an X-ray tube. The positions of the lines in the characteristic radiation are determined solely by the material of the anticathode from which they arise; the wave length limits of the white radiation and the distribution of intensity within these limits, on the other hand, depend also upon the voltage impressed on the tube. The continuous radiation does not gradually become less and less intense until the central image of zero diffraction, and zero wave length, is reached but has a definite short wave length limit (Figure 54).

This observation,[2] which is confirmed by accurate measurement upon photographs and with other indicating devices, provides the opportunity.

[1] W. L. Bragg, Proc. Camb. Phil. Soc. *17*, 43 (1912).
[2] W. Duane and F. S. Hunt, Phys. Rev. *6*, 166 (1915).

of determining the wave length of X-rays through the application of quantum principles. The energy of the fastest moving electrons striking the target is measured by the product of the voltage V′ applied to the tube and the charge e on the electron. If the frequency ν of the excited

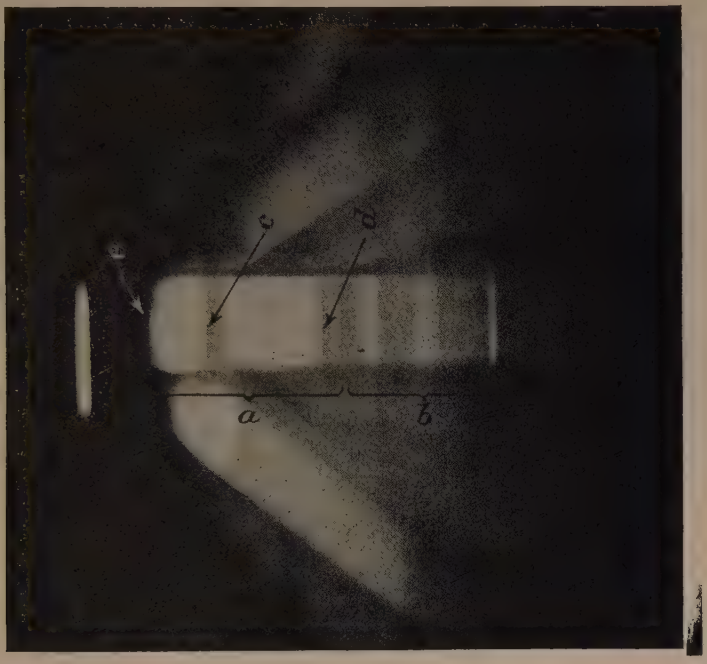


FIG. 54.—The spectrum obtained from tungsten with an impressed voltage of about 50,000 volts, the cleavage face of calcite being used as "reflector." The region included within *a* is continuous white radiation; *b* designates the L-series characteristic lines. The critical absorption limit for silver (in the first reflected order) is marked *c*, that for bromine is marked *d*. The spectrum stops sharply at *e*.

rays corresponding to this limit is connected with the energy E through the quantum relation $E = h'\nu$, then

$$V'e = E = h'\nu \quad . \quad . \quad .

the characteristic radiation of an element.[1] It has already been pointed out that this radiation consists of a series of sharply defined lines. Experiment shows that when the voltage is increased beyond a point for which the corresponding energy in the electron stream is too low to excite any characteristic radiation, a point finally will be reached at which all of these lines will flash out together.[2] If the minimum energy requisite for the production of such a spectrum is made equivalent to the frequency of the shortest characteristic line to appear, frequency values will result which are a fraction of one per cent less than those calculable from the low wave length limit of the continuous spectrum.[3]

The first determination[4] of the wave length of X-rays was obtained through spectrum observations upon sodium chloride and allied crystals. As already stated, the connection between the angle of reflection from a cube (100) face of sodium chloride, the wave length of the "reflected" X-rays and the spacing normal to the "reflecting" face is given by the expression $n\lambda = 2\, d_{100} \sin\theta$. The spacing between geometrically like cube faces is equal to the length of the edge of the unit cube. The volume V of the unit must be the product of the mass of a single chemical molecule of sodium chloride (NaCl) multiplied by the number of these molecules (m) associated with the unit cell and divided by the density ρ of the salt. In other words:

$$(d_{100})^3 = \frac{mM}{\rho} = V$$

substituting this value of d_{100} in expression (2):

$$n\lambda = 2\sqrt[3]{\frac{mM}{\rho}} \sin\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If now it is assumed that sodium chloride has an atomic arrangement the unit cell of which is shown in Figure 55 (cf. Figure 47), m will equal four. Since the plane parallel to the cube face midway between the two sides of the unit cell (OABCDEFG) is physically identical with the planes bounding the unit cube, n will equal two for the first reflection to appear at the angle θ. The mass of the hydrogen atom, and hence of the sodium chloride molecule, is known from Avogadro's number and the value for λ is therefore immediately determinable. The results from this determina-

[1] W. H. Bragg, op. cit.; W. H. and W. L. Bragg, X-rays and Crystal Structure (London, 1918), Chap. VI.

[2] This is strictly true only of the lines of the K-series. The longer wave length characteristic radiations are emitted in three or more groups rather than at once. The arguments presented here apply equally well to the shortest wave length component of each of these groups.

[3] D. L. Webster, Phys. Rev. 7, 599 (1916).

[4] W. H. Bragg, op. cit.

tion are in agreement with those based upon the quantum calculations. As a conclusive fixing of the wave length this method is unsatisfactory [1] because of its fundamental assumption of a structure for sodium chloride. Its agreement with quantum conditions, however, especially when combined with its successful application to many other crystals and in other fields of X-ray study leaves little doubt of the correctness of the absolute wave lengths thus assigned to X-rays.

The lengths of the X-rays produced under ordinary conditions range from about 2.50 A° to about 0.06 A°. An Angstrom Unit (1 A°) is 1×10^{-8} cm. X-rays as long as 14 A° have been measured by the spectroscopic method that has been outlined; some γ-rays, considered to be very short X-rays, have lengths that probably are of the order of 0.01A°. A

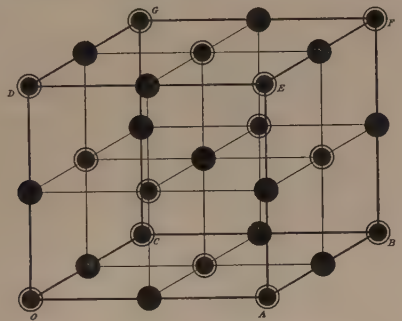


FIG. 55.—The unit cell of the sodium chloride arrangement of atoms. The positions of one kind of atom are represented by ringed circles, of the other by black circles. This unit cell OABCDEFG is strictly analogous to the corresponding units of Figs. 47, 48, etc.

picture of the length of these waves is furnished by remembering that λ for visible light ranges between about 7800 A° and 4000 A°.

Before the wave lengths of X-rays could be directly studied through spectroscopic observations (Figure 53) their quality was measured by their "hardness" or penetrability for some standard substance, usually taken as metallic aluminum or copper.

It is now recognized that, other things being equal, "harder" rays have a shorter wave length.

X-Rays Produced by Different Elements. *Characteristic Radiation.*— The characteristic (line) spectra of the elements have been carefully studied and measured.[2] The radiations producing them presumably arise from changes in the energy content of atoms and thus are primarily

[1] R. W. G. Wyckoff, J. Wash. Acad. Sci. *11*, 366 (1921).
[2] Especially by M. Siegbahn et al. All of these data of use in crystal analysis are collected by W. Duane, Bull. Nat. Research Council *1*, No. 6 (1920).

atomic, as opposed to molecular, phenomena. In accordance with this conclusion it has invariably been found that the X-ray spectrum from a compound is almost exactly the simple sum of the spectra of its component elements.

Four distinct series of line spectra for an element have been discovered. They are usually designated as the N-series, the M-series, the L-series and the K-series.[1] For a particular atom the N-series lines have the longest, the M-series lines shorter, the L-series lines still shorter, and the K-series lines the shortest wave lengths. Each of these series consists of relatively few lines. The same lines occur from different elements, with progressively altered wave lengths (Figure 56). In passing from element to element in the direction of increasing atomic number the wave lengths of a line in a series decrease in a regular fashion. By plotting the square root of the frequency, $\sqrt{\nu}$, of corresponding lines against atomic numbers (N), a group of nearly straight lines will be obtained.[2] The many relations that have been found to exist between lines in the same series and different series find extensive use in the development of theories of atomic structure.[3]

It has been said that the K-series spectra will be emitted when and only when the impressed voltage is at least a fraction of one per cent greater than that which corresponds, by the quantum relation, to the frequency of the shortest K-line. The wave length with an energy equivalent through the quantum relation to this critical voltage may be called the quantum wave length.[4] If the voltage is above this value for an element which displays all four series then the characteristic spectrum of the element will consist of not only the K-lines but those of the L-, M- and N- series as well. Whereas the K-series lines are called into being together, the L-series has three and the M-series possibly five critical voltages. With increasing potential across a tube the N-series lines would first make their appearance, probably in several sections, to be followed by the five (?) parts of the M-series, the three parts of the L-series and finally by the K-lines. It would thus be possible by an appropriate adjustment of voltage to produce only a portion of the L-, M- or N-series of an element but the K-series spectrum must be had either in its entirety or not at all.

All four series are not found for most atoms. N-series lines have yet been observed from only a few of the heaviest elements. The M-lines have been observed from the elements from dysprosium (atomic number

[1] Recently a few O-series lines have been measured.
[2] H. G. J. Moseley, Phil. Mag. *26*, 1024 (1913); *27*, 703 (1914).
[3] See A. Sommerfeld [H. L. Bose, translator], Atomic Structure and Spectral Lines, 3d Edition, 1923.
[4] W. Duane, op. cit.

= 66) to uranium (atomic number = 92). The L-series has been measured for zinc and all of the heavier elements. Spectra in the K-series are recorded from sodium to platinum.

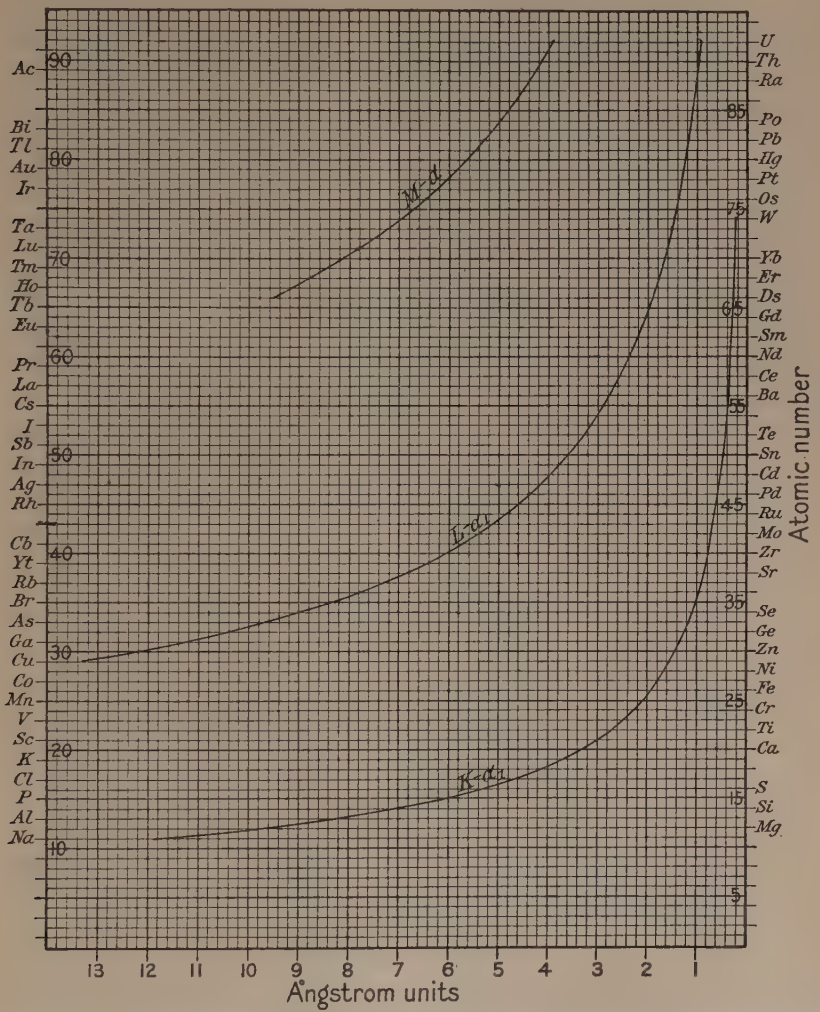


FIG. 56.—In this figure atomic numbers are plotted as ordinates and the wave lengths of the strongest lines in each of the characteristic series as abscissas.

In studying the structures of crystals it is necessary to know accurately the wave lengths of the characteristic X-rays from elements that are used as targets in X-ray tubes. The present practice in making anticathodes usually employs either tungsten or molybdenum although rhodium,

palladium, platinum, iridium and sometimes brass, copper and iron may be encountered. The wave lengths in the spectrum of these substances and a few other useful elements are given in Tables I and II.

TABLE I. WAVE LENGTHS OF K-SERIES LINES OF SOME ELEMENTS

ELEMENT	AT. NO.	α_2	α_1	β_1	γ
Iron	26	1.932A°	1.9324	1.7540	1.736
Copper	29	1.543	1.5374	1.3889	1.382
Zinc	30	1.437	1.433	1.294	1.281
Bromine	35	1.040	1.035	0.929	0.914
Zirconium	40	0.793	0.788	0.705	—
Molybdenum	42	0.7121	0.7078	0.6311	0.6197
Ruthenium	44	—	0.645	0.574	—
Rhodium	45	0.6164	0.6121	0.5453	0.5342
Palladium	46	0.500	0.586	0.521	—
Silver	47	0.567	0.562	0.501	0.491
Cadmium	48	0.543	0.538	0.479	—
Tin	50	0.490	0.487	0.432	—
Iodine	53	—	0.437	0.388	—
Tungsten	74	0.2134	0.2086	0.1842	0.1790

NOTE: The data of this and the following table have been taken from W. Duane, op. cit.

The General or "White" Radiation. — Less of a quantitative nature [1] is known about the continuous X-ray spectrum obtained from metals acting as anticathodes. Its general character is shown by the intensity-wave length curves of Figure 57. With increasing wave length the intensity rises rapidly from zero to a more or less pronounced maximum, after which it drops again to a small value. The quantum conditions which determine the short wave length zero-point for different voltages have been discussed (page 68). Measurements of intensity distribution curves at various voltages, the same power being applied to the tube in every case, show (Figure 58) that not only does the "white" radiation become more intense the higher the voltage but its maximum likewise becomes more pronounced and is shifted at the same time towards shorter and shorter wave lengths. These phenomena for the general radiation from tungsten are probably typical of those from other metals. The curves of Figure 57 were prepared from tubes operated at 35,000 volts with a constant power consumption; nevertheless not only their shapes but also the absolute amount of continuous radiation for different elements are widely unlike. The curve for molybdenum gives an idea of the

[1] The following data are taken from papers by C. T. Ulrey, Phys. Rev. *11*, 401 (1918), and H. Kulenkampff, Ann. d. Physik *69*, 548 (1922).

TABLE II. WAVE LENGTHS OF L-SERIES LINES OF SOME ELEMENTS

ELEMENT	AT. NO.	l	α_2	α_1	η	β_4	β_1	β_2	β_3	β_5	γ_1	γ_2	γ_3	γ_4
Tungsten	74	1.675A°	1.484	1.473	1.4177	1.298	1.279	1.2419	1.260	1.2031	1.095	1.0658	1.059	1.026
Iridium	77	1.540	1.360	1.350	—	1.176	1.154	1.133	1.138	1.101	0.989	0.962	0.956	0.917
Platinum	78	1.499	1.323	1.313	1.242	1.142	1.120	1.101	1.098	1.072	0.958	0.933	0.929	0.900
Gold	79	1.457	1.283	1.271	1.197	1.102	1.080	1.065	1.059	1.035	0.922	0.898	0.894	0.869
Lead	82	1.348	1.186	1.175	1.091	1.008	0.983	0.983	0.968	—	0.842	0.820	0.816	0.792

relative intensity of the characteristic K-lines at this voltage compared with the surrounding "white" X-rays. The total amount of continuous radiation, and the intensity of its maximum, are evidently greater the

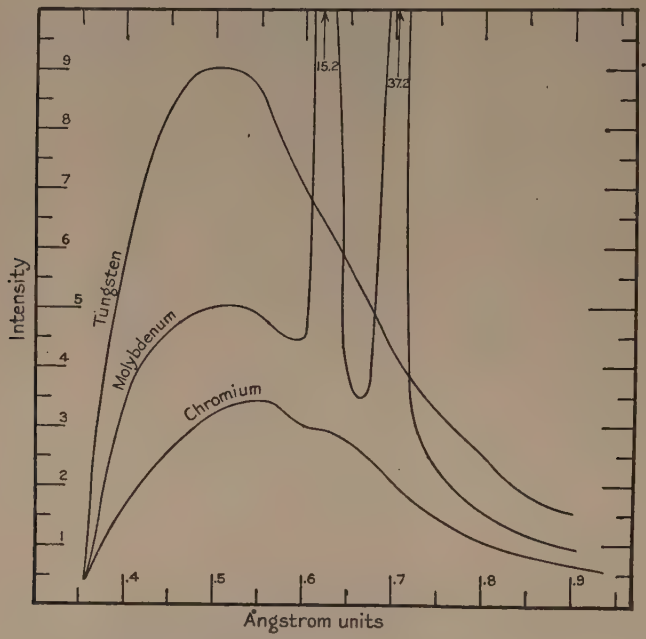


FIG. 57.—A plot of intensity against wave length for X-rays from targets of three typical metals. The applied voltage was 35,000 volts in each instance. (After C. T. Ulrey, op. cit.).

TABLE III. DATA SHOWING THE EXTENT TO WHICH THE INTENSITIES OF THE MAXIMA OF THE WHITE RADIATION FROM DIFFERENT ELEMENTS AND THE TOTAL RADIATION FROM THESE ELEMENTS ARE PROPORTIONAL TO THEIR ATOMIC NUMBERS

ELEMENT	ATOMIC NUMBER	TOTAL RADIATION		INTENSITY OF MAXIMUM OF THE WHITE RADIATION
		Ulrey	Kulenkampff	
Platinum	78	78 units	80.5 units	77.5 units
Tungsten	74	70.2	—	—
Tin	50	—	52.8	51.2
Silver	47	—	48.2	47.5
Palladium	46	47	—	—
Molybdenum	42	42.3	—	—
Copper	29	—	29.0	29.0
Nickel	28	35.6	—	28.0
Cobalt	27	—	—	27.1
Iron	26	—	—	25.9
Chromium	24	27	—	—
Aluminum	13	—	11.5	11.8

higher the atomic number of the anticathode. Measurements [1] of the total radiation for voltages from 19,000 to 41,000 volts from targets of copper, nickel, cobalt and iron seem to show not only an increase of radiation with atomic number, instead of atomic weight, but a proportionality between the two. The areas under the intensity curves arising from one

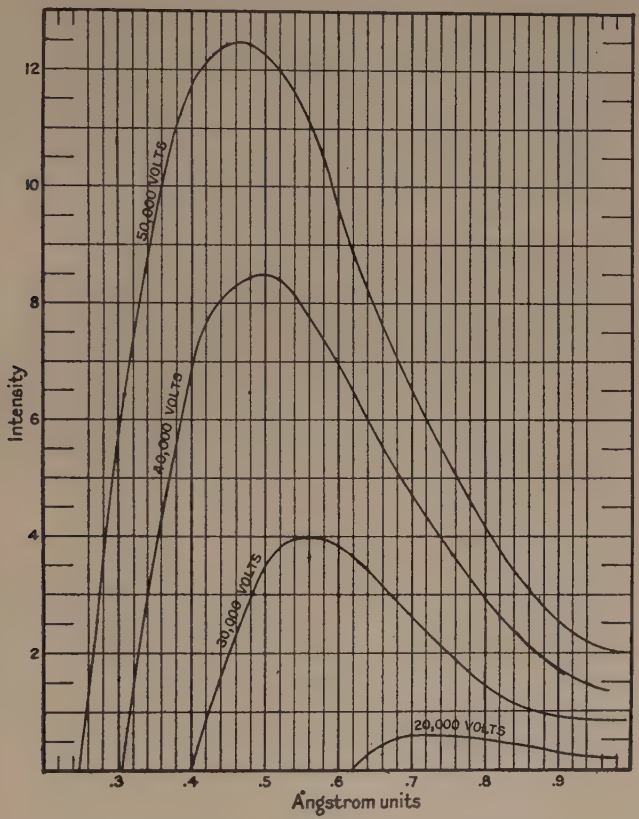


FIG. 58.—Curves showing the distribution with wave length of the continuous radiation from tungsten at several voltages. (After C. T. Ulrey, op. cit.).

set of observations [2] do not show such an exact proportionality (Table III and Figure 59) but more recent experiments [3] (made at about 10,000 volts), in which corrections were introduced for the amount of absorption in the target, indicate that not only the total radiation but the intensity of the

[1] W. Duane and T. Shimizu, Phys. Rev. *11*, 491 (1918).
[2] C. T. Ulrey, Phys. Rev. *11*, 401 (1918).
[3] H. Kulenkampff, Ann. d. Physik *69*, 548 (1922); E. Wagner and H. Kulenkampff, Physikal. Z. *23*, 503 (1922).

maximum of the continuous region is closely proportional to the atomic number (Table III and Figure 59).

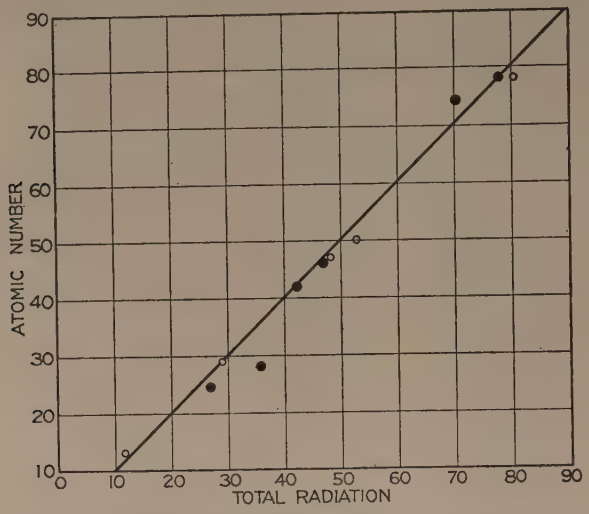


FIG. 59.—Plots of data recorded in Table III showing the variation of the total radiation with change in the atomic number of the target. The black circles are measurements by Ulrey (op. cit.), the open circles are those by Kulenkampff (op. cit.).

Absorption of X-rays and the Reëmission of Secondary Radiation

In spite of their most striking property being the ability to penetrate otherwise opaque substances, X-rays of all wave lengths are absorbed to some extent in passing through any substance. It has been shown that with monochromatic rays the fraction absorbed is the same for equal thicknesses of the absorber. This is the same law that holds for the absorption of ordinary light in an imperfectly transparent medium, namely:

$$I = I_0 e^{-\mu x''} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where I is the amount of the transmitted radiation, I_0 is its original intensity, x'' is the thickness of the absorbing medium and μ is a constant, the so-called absorption coefficient. Another constant, μ/ρ, the mass absorption coefficient, is obtained by modifying this equation through the introduction of the density ρ of the absorbing substance so that

$$I = I_0 e^{-\mu/\rho \cdot \rho x''} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This coefficient is particularly important in working with the absorption of X-rays because it has been found to be a constant for a particular substance irrespective of its physical state. Thus a compound will have the

same mass absorption coefficient, though of course not the same absorption coefficient, whether it is a solid, a liquid or a gas. This is equivalent to the statement that the amount of the absorption of X-rays is conditioned by the amount of matter in their path. It is a corollary of this fact that the absorption is independent of the state of chemical combination: hence the opacity of a chemical compound can be calculated directly from the absorptions of its constituent elements.

A considerable portion of the energy absorbed when X-rays strike a body is emitted again as X-radiation. These rays that are produced not by the direct bombardment of a substance by electrons but through the action of X-rays themselves are called secondary X-rays.[1] Secondary X-rays are of various kinds and arise as a result of several distinct processes taking place within the absorbing body.

Some of the primary X-rays on striking the atoms of the absorber seemingly put electrons into a state of forced vibration with the consequent emission of *scattered X-rays*. It has been supposed that the wave lengths of these scattered rays are identical with those of the radiation producing them; recent experiments,[2] however, seem to show that at least some of them are slightly softer. These purely scattered rays bear definite phase relationships to the wave producing them and interference effects are possible between them.

Most of the energy of absorbed X-rays goes towards the liberation of electrons from atoms of the absorber. Under favorable conditions some of these appear as photo-electrons but most strike other atoms and either dissipate their energy as heat or give rise to X-rays, as in the production of primary radiation. Characteristic rays from elements in the absorber will be obtained if the energy (the $h\nu$ value) of the incident X-rays is sufficiently great. Stokes' law, that secondary or fluorescent radiation can never have a wave length shorter than the rays which produce it appears to hold universally for X-rays. This fact combined with the realization that all of the lines in a series, or sub-series for the L- and M-spectra, are produced at one time leads to the rule that secondary characteristic radiation from an element of an absorbing substance will be set up by incident X-rays of wave lengths equal to or shorter than the quantum wave length (page 72) for a series or sub-series. The shortest line in the K-series spectrum from molybdenum, for instance, has a wave length of 0.6197A° (Table I); consequently when shorter X-rays than this strike upon molybdenum they will call forth the lines of its K-series.

[1] Data upon properties of secondary X-radiations have been assembled by A. H. Compton, Bull. Nat. Research Council *4*, No. 20 (1922).

[2] A. H. Compton, op. cit.; P. A. Ross, Proc. Nat. Acad. Sci. *2*, 246 (1923). Still more recent experiments have failed to find this change of wave length [G. L. Clark and W. Duane, Proc. Nat. Acad. Sci., Dec. (1923)].

Rhodium is the element that has strong K-lines (α_1 and α_2 in Table I) lying nearest to this wave length on the high frequency side; and consequently secondary K-radiation of molybdenum will be produced by the X-rays from a tube with a target of rhodium or a metal heavier than rhodium. It has customarily been supposed that no phase relationships exist between the secondary rays produced in a crystal and that consequently these rays would result in only a generally distributed fogging. This is unquestionably true of most of them and the possibility of their being produced within the crystal under investigation must always be taken into account. They must also be considered in the choice of materials to serve as absorbing agents and in the design of spectrometers and other measuring instruments. In recent experiments [1] with white X-rays, however, an especially strong reflection has been found of wave

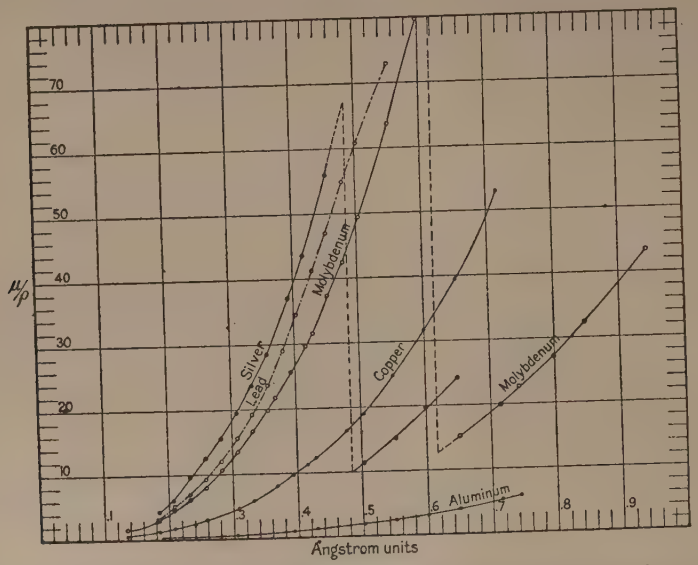


FIG. 60.—Curves for typical metallic absorbers showing the mass absorption coefficients (uncorrected for scattering) at various wave lengths. (Data of F. K. Richtmyer, op. cit.).

lengths characteristic of atoms in the reflecting crystal. As yet the properties of this "characteristic reflection" are incompletely understood; but its very existence and the opportunity it offers of producing distinctive diffraction effects from only a part of the atoms of a crystal make it of immediate interest and probably of great future value to crystal analysis (see also page 159).

[1] G. L. Clark and W. Duane, Proc. Nat. Acad. Sci. *9*, 126 (1923); J. Opt. Soc. Am. *7*, 455 (1923); G. Mie, Zeit. f. Physik *15*, 56 (1923).

A general parallelism is observed between the intensity of secondary X-ray emission and the amount of absorption. The phenomena of X-ray absorption can be shown by plotting μ/ρ against wave length for several typical absorbing substances [1] (Figure 60). Except for marked discontinuities at certain positions the absorption decreases with a decrease in the wave length of the incident X-rays. When not in the region of these discontinuities the absorption for the same wave length increases with the atomic number of the absorber. There is a large production of secondary characteristic radiation from an absorber whenever the critical quantum wave length (page 72) of a series is equaled and passed (in the direction of increasing frequency). Commensurate increases should therefore be observed in the absorption at these wave lengths and investigation shows that the sudden increases in absorption that are observed following the normal decrease with shortening wave length always occur at points which are the same to within a fraction of one per cent as the longest wave capable of exciting secondary characteristic radiation in the absorber (the quantum wave length). It is, for instance, a consequence of this relation that molybdenum (which requires for the excitation of its K-lines any wave length shorter than about 0.6197A°) is the proper absorbing

TABLE IV. SOME CRITICAL ABSORPTION LIMITS (K-SERIES) [2]

ELEMENT	ATOMIC NUMBER	ABSORPTION LIMIT
Iron	26	1.7396A°
Copper	29	1.3785
Zinc	30	1.2963
Bromine	35	0.9179
Zirconium	40	0.6872
Molybdenum	42	0.6184
Ruthenium	44	0.5584
Rhodium	45	0.5330
Palladium	46	0.5075
Silver	47	0.4850
Cadmium	48	0.4632
Tin	50	0.4242
Iodine	53	0.3737
Tungsten	74	0.1781

substance to use if one desires to absorb selectively the K-radiation from rhodium, with a longest wave $\alpha_2 = 0.6164$A°, but let any longer waves which may be present in the X-ray beam pass through with little change. Similarly an inspection of Table IV shows that all lines in the spectrum of molybdenum shorter than the two most intense lines α_1 and α_2 (Table I)

[1] These data are given by F. K. Richtmyer, Phys. Rev. *18*, 13 (1921).
[2] These data are taken from tables given by W. Duane, Bull. Nat. Research Council *1*, No. 6 (1920).

can be strongly absorbed if zirconium is used. Table IV states the K-series critical absorption limits for those elements which find most common use in crystal structure study.

Discontinuities in absorption occur in the region of the L-radiation but, whereas the break is a single one for the K-series, three distinct increases in absorption are to be noted in this longer wave length region [1] (Figure 61). This is in agreement with the observation that the L-series

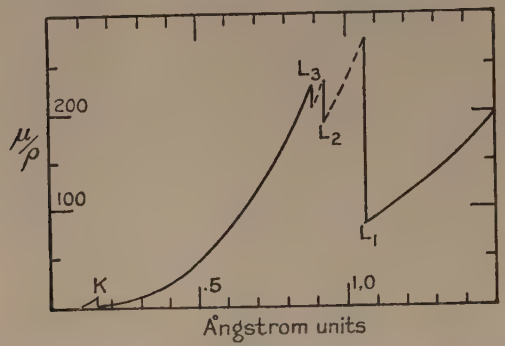


FIG. 61.—The probable absorption curve for platinum at different wave lengths. (After A. H. Compton, op. cit.).

is a complex one capable of being excited in three separate portions and thus possessing three different critical emission wave lengths.

Because the energy absorbed when X-rays impinge upon matter is devoted to several different processes, the mass absorption coefficient of equation (6) can be considered as a composite thing with one term given over to each process:

$$\frac{\mu}{\rho} = \frac{\mu_1}{\rho} + \frac{\mu_2}{\rho} + \frac{\mu_3}{\rho} + \ldots$$

Thus far in treating X-rays of ordinary wave lengths it has been customary merely to separate μ/ρ into two terms. One of these, σ/ρ, is the mass scattering coefficient; the other, μ'/ρ, the "true" mass absorption coefficient, takes care of the rest of the absorption. Thus:

$$\frac{\mu}{\rho} = \frac{\mu'}{\rho} + \frac{\sigma}{\rho} \quad \ldots \ldots \ldots \quad (7)$$

This division permits of a reasonably good quantitative calculation of absorptions except in the regions immediately below critical absorption wave lengths.

[1] This figure, which represents the probable absorption of platinum, is copied from A. H. Compton, Bull. Nat. Research Council *4*, No. 20 (1922).

Numerous attempts have been made to formulate both the mass scattering and the mass absorption coefficients in terms of the wave length of X-rays and the atomic weight or the atomic number of the absorbing element. It has been shown [1] that if the atomic dimensions were negligible the mass scattering coefficient, σ/ρ, would be constant for all atoms and equal to about 0.20. The observed scattering, however, is variable, being greater for heavy than for light atoms and becoming very small for X-rays of extremely short wave lengths. For practical calculations of the absorbing power of materials the scattering is relatively so slight that it may be neglected for all but the lightest of elements.

Studies of the absorption of X-rays of different wave lengths by a single substance have given rise to the expression[2]

$$\frac{\mu}{\rho} = K\lambda^3 + \frac{\sigma}{\rho}.$$

K is a constant for the absorbing material in a region between two absorption limits; but its value is radically different on opposite sides of one of these limits. This constant apparently can be related to the atomic number of the absorbing atoms in the following manner. The term μ'/ρ of the equation

$$I = I_0 e^{-\mu/\rho \cdot \rho x''} = I_0 e^{-(\mu'/\rho + \sigma/\rho)\rho x''} \quad . \quad . \quad . \quad . \quad (6a)$$

is a coefficient of $\rho x''$ which is itself a measure of the number of grams per square centimeter of the absorber. If this μ'/ρ is multiplied and divided through by the number of atoms in a gram, N'/M', where N' is the number of atoms in the gram atom (6.06×10^{23}) and M' is the molecular weight of the absorber, there will result:

$$\left(\frac{\mu'}{\rho} \cdot \frac{M'}{N'}\right) \times \frac{N'}{M'} = \mu_a \cdot \frac{N'}{M'} \text{ and } I_0 = I_0 e^{-\mu_a (N'/M')\rho x'' - (\sigma/\rho)\rho x''} \quad . \quad . \quad . \quad (8)$$

The term $(N'/M')\rho x''$ measures the number of atoms per square centimeter of the absorber and its coefficient, μ_a, is called the atomic absorption coefficient.[3] For absorptions that are calculated in terms of atomic absorption coefficients, the data suggest that [4]

$$\mu_a = \kappa N^4 \lambda^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In this expression N is the atomic number and κ is a universal constant which has the value 2.29×10^{-26} on the short wave length side of the

[1] J. J. Thomson, Conduction of Electricity Through Gases, 2d Edition.
[2] For instance, see W. Duane and F. S. Hunt, Phys. Rev. *6*, 166 (1915).
[3] It is frequently the custom to include the scattering coefficient within the atomic absorption coefficient. For the present purposes, at least, that procedure is not of advantage.
[4] F. K. Richtmyer, op. cit.

K-absorption limit and (less accurately) 0.33×10^{-26} on the other. The relatively few substances for which this expression has been tested fit with a considerable degree of accuracy except on the short wave length

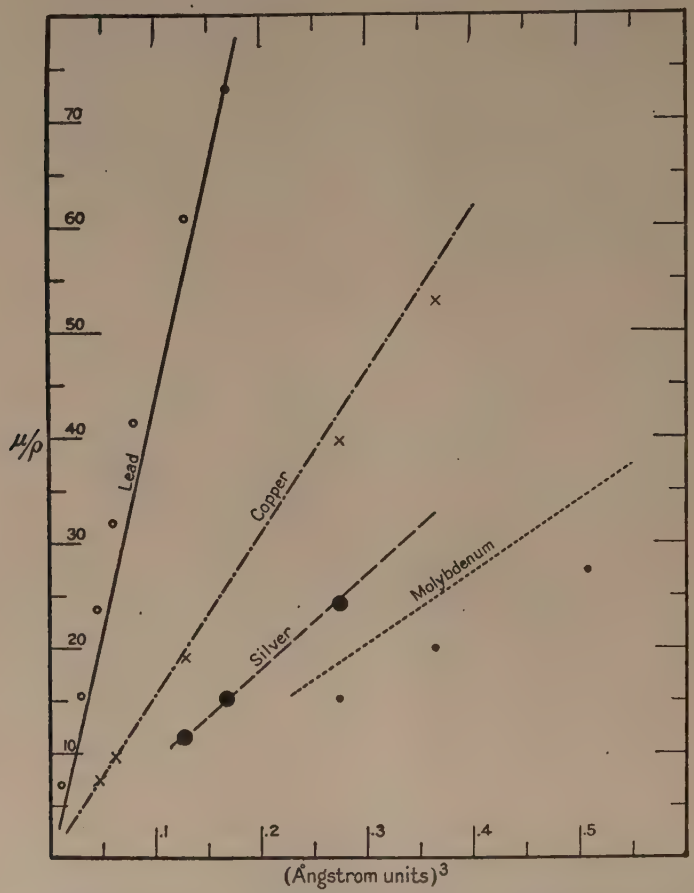


FIG. 62.—The absorption lines of this figure have been calculated through the use of expressions (7) and (8).

edge of a critical absorption limit. The calculated absorption coefficient is then uniformly too great. Bearing their limitations in mind, expressions (8) and (9) can nevertheless be used to calculate the approximate amount of absorption to be anticipated from a given thickness of any element. A general idea of their correctness may be obtained [1] from Figure 62.

[1] The experimental data for this figure are taken from F. K. Richtmyer, op. cit.

If the absorbing substance is a chemical compound instead of a single element its mass absorption coefficient can be calculated from the coefficients of its constituent atoms by compounding them with due respect to the relative amounts by weight of different elements that are present. Thus, if $(\mu/\rho)_C$ and $(\mu/\rho)_D$ are the mass absorption coefficients of two elements with the atomic weights c and d respectively, the mass absorption coefficient of the compound CD will be [1]

$$\left(\frac{\mu}{\rho}\right)_{CD} = \left[c\left(\frac{\mu}{\rho}\right)_C + d\left(\frac{\mu}{\rho}\right)_D\right] \Big/ [c + d]$$

In view of the approximate character of the results of the absorption calculations now possible, it is fortunate for crystal structure work that in its present stage of development more accurate information is not required. For many purposes, such as the determination of the proper thicknesses of absorbing screens for waves of a particular length or the calculation of the relative effects of rays of different wave lengths upon the photographic plate, some idea of the amount of absorption taking place is essential. When the physical knowledge upon which determinations of crystal structure are made becomes more exact and quantitative measurements of the amount of X-rays scattered in different directions become possible, it will be necessary to know, for instance, (1) the amount of X-rays absorbed in passing in a particular direction through a section of crystal of known thickness, or (2) the amount of X-rays of a particular wave length that are absorbed by a known thickness of the sensitive silver bromide emulsion of a photographic plate.

The phenomena of selective absorption give to all photographs of X-ray spectra a distinctive appearance. The photographic effect of X-rays is apparently proportional to their absorption in the sensitive emulsions of the plate.[2] Rays that are most strongly absorbed by either bromine or silver hence will produce the greatest blackening. The regions of the K-selective absorption for both silver and bromine occur in the range of the strong continuous radiation in the spectrum of Figure 54 and give it a banded appearance which does not at all correspond to the actual energy distribution (see Figure 58). This fact greatly increases the difficulties of attempting to measure X-ray intensities by a photographic method. The same sort of undue stressing of some wave lengths at the expense of others will also be found in working with an ionization chamber which does not absorb all of the X-rays incident upon it especially when in the neighborhood of the characteristic regions of the absorbing gas. On the other hand it obviously is of great advantage to use X-rays that will be

[1] R. Glocker, Physikal. Z. *19*, 66 (1918).
C. G. Barkla and G. H. Martyn, Phil. Mag. *25*, 296 (1913).

selectively absorbed by the sensitive materials of the indicating device whenever faint effects are to be sought.

The Scattering Power of Atoms for X-rays

The diffraction effects which have furnished an indication of the manner of arrangement of atoms in various forms of matter and which will be discussed in the remainder of this book are produced by scattered X-rays. Knowledge of the laws governing this scattering thus is of vital concern to the subject of crystal analysis. It is unfortunately true that little exact knowledge of their nature is yet available. This is due not only to the complexity of the phenomena producing scattering but to the experimental difficulties of its accurate measurement. If it is assumed that (1) classical dynamics may be applied, (2) the constraining forces acting upon an electron need not be considered, (3) interelectronic distances in the atom are so small that each electron scatters independently of the others, and (4) the electrons may be considered as point charges, then the intensity of scattering (I_s) per unit volume has been calculated to be

$$I_s = I_0 \frac{NN'e^4(1 + \cos^2 2\theta)}{2m'^2 L^2 c'^2} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

In this equation [1] N is the number of electrons in the atom (the atomic number); N′ is the number of atoms in the unit volume; I_0 is the intensity

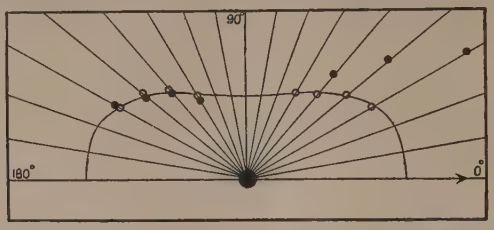


FIG. 63.—The heavy curve shows the variation of scattering with angle which is to be expected from expression (10). The black circles record experimental data upon soft X-rays, the open circles upon moderately hard radiation. (After A. H. Compton, op. cit.).

of the original beam; e, m′ and c′ have their customary significance of the charge and mass of the electron and the velocity of light respectively; L is the distance between the measuring device and the scattering material; and 2θ is the angle which the scattered beam makes with the primary X-rays.

This equation is in only very approximate agreement with experiment. A comparison of its requirements with the observed scattering of both

[1] J. J. Thomson, op. cit., p. 321.

soft X-rays and rays of moderate hardness by filter paper is given in Figure 63.[1] At right angles to the direction of propagation of the incident X-rays the agreement is excellent but for small angles the observed scattering is too great.[2] This excess of scattering over that required by (10) is

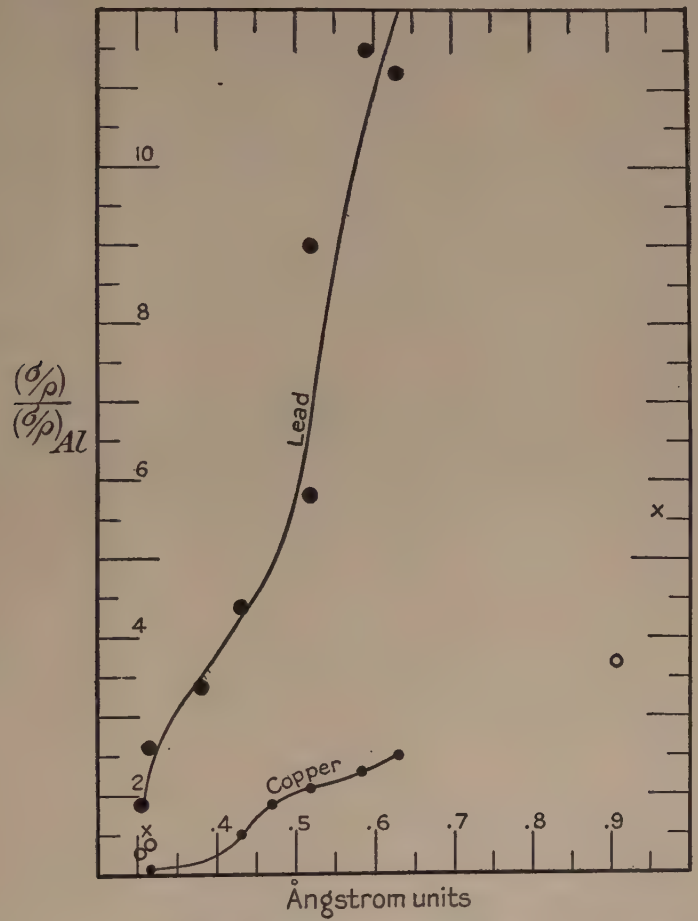


FIG. 64.—In this figure the ratios of the mass scattering coefficients of several elements and of aluminum (all measured at right angles to the direction of propagation of the X-rays) are plotted for various wave lengths. If equation (10) were accurate all of the points of these curves would lie on the axis of abscissas. Crosses represent observations upon tin and open circles measurements upon silver.

[1] This figure is taken from A. H. Compton, Bull. Nat. Research Council *4*, No. 20 (1922). The data are from E. A. Owen, Proc. Cambr. Phil. Soc. *16*, 161 (1911). These soft X-rays probably corresponded to a beam in which most of the radiation lay between 0.50A° and 1A°; the corresponding limits for the medium rays probably were 0.25A° and 0.50A°. (A. H. Compton, op. cit.)

[2] Experiments upon aluminum [A. R. Duane and W. Duane, Phys. Rev. *20*, 86 (1922)] and various liquids [C. W. Hewlett, Phys. Rev. *20*, 688 (1922)] indicate that for very small angles the scattering becomes vanishingly small.

greater for longer wave lengths and heavier elements. The data of Figure 64, wherein the ratio of the scattering of equal masses of various metals and of aluminum (as a standard) are plotted against wave length, show this clearly.[1]

The fact that equation (10) gives an agreement with experiment under any circumstances has been taken as evidence for its fundamental correctness. Of the various assumptions used in its deduction the third, that inter-electronic distances in atoms are so small that each electron scatters independently of the others, is the most vulnerable one. By making the necessary assumptions concerning electronic distances in the atoms and their interaction during scattering, the experimental data of Figures 63 and 64 have been calculated from an appropriate modification of (10)[2]; it is not now evident what significance attaches to such agreement.[3] It is certain, however, that much more work, both experimental and theoretical, is necessary before the laws of scattering can be considered as even approximately known.

[1] This figure is drawn from the data of C. G. Barkla and J. G. Dunlop, Phil. Mag. *31*, 222 (1916). They have also shown that over the region of wave lengths employed the mass scattering coefficient of aluminum remains substantially constant.

[2] A. H. Compton, op. cit.

[3] Very recently an hypothesis of scattering, based upon quantum principles, has been proposed [A. H. Compton, Phys. Rev. *21*, 483 (1923)].

Chapter III. The Interaction of X-rays and Crystals

Introduction

Since crystals are composed of regularly distributed atoms which can act as scattering centers, diffraction effects may be expected from their interaction with X-rays having wave lengths comparable with the interatomic distances. The nature of these effects depends upon the kinds and positions of the atoms in a crystal; consequently the theory which describes them in terms of atomic positions forms the basis of studies of crystal structure using X-rays.[1]

A complete theory would develop in detail expressions to describe the diffraction patterns resulting from any conceivable arrangement of atoms. The solution of the problem in this general form, unfortunately, is accompanied by analytical complexities which add little to an understanding of the requisite physical assumptions. For this reason it seems advisable to outline an approximate treatment of only the mathematically simplest case of cubic crystals. The modifications in the expressions thus obtained when they are applied to other than cubic crystals will, however, be stated.

Diffraction effects are characterized by both position and intensity. It will be shown that the first of these can be completely and exactly predicted but at the present time even relative intensities can only be approximately foretold.

The Positions of X-ray Diffraction Effects from Crystals

The[2] points of the row A_1, A_2, A_3, . . . A_s of Figure 65 are separated by the constant interval $A_1A_2 = A_2A_3 = e$. It will be assumed that these points can act as diffracting centers for a parallel beam of rays C_1D_1, . . .

[1] A direct mathematical treatment of the positions and intensities of X-ray diffraction effects in terms of the positions of diffracting atomic centers has been given by M. Laue, notably in Jahrb. Rädioakt. u. Elektronik *11*, 308 (1914); and in Encyclop. der Math. Wiss. Bd. V., Art. 24, Wellenoptik. Other methods of calculation which usually follow the reflection analogy but differ somewhat from the procedure to be described in this chapter in the form and derivation of their expressions have been employed from time to time. Notable among these is the procedure (based in part upon geometrical concepts stated by S. Kreutz, Krystallstruktur, Leipzig, 1915) which is outlined by P. Niggli, Geometrische Krystallographie des Discontinuums, Leipzig, 1919.

[2] The treatment at this point is closely similar in form to that used by A. Sommerfeld, Atombau u. Spektrallinien, Chapter III, Sec. 1 (Braunschweig, 1922).

The difference in path, and consequently the retardation of the ray C_1C_2, diffracted by A_1, compared with the ray D_1D_2 is e $(\delta - \delta_0)$, where the direction cosine of the incident beam (with respect to the row $A_1 \ldots A_s$) is $\delta_0 = \cos \angle A_1A_2D_1 = A_2B_2/e$ and that of the diffracted ray is $\delta = \cos \angle C_2A_1A_2 = A_1E_1/e$. If this path difference is equal to their wave length, or some integral multiple thereof, reinforcement will take place between the two rays; otherwise with an extended row of diffracting centers there will always be destructive interference, between neighboring points if

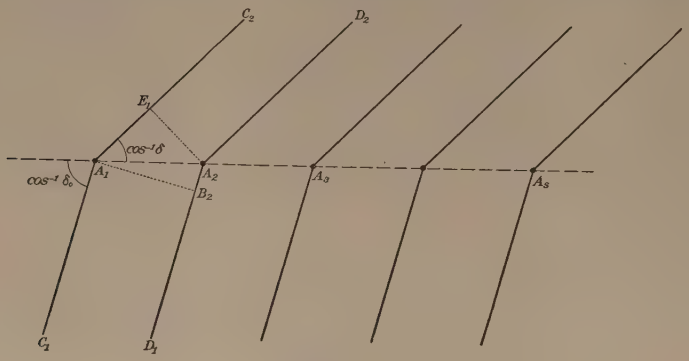


Fig. 65.

the waves are exactly out of phase, or between more distant atoms for some other phase difference. If λ is the wave length of the diffracted waves and h_0' is some integer, then constructive interference will be observed when

$$e(\delta - \delta_0) = h_0'\lambda \quad \ldots \ldots \ldots \ldots \ldots \quad (11)$$

This is essentially the state of affairs that holds for a simple line grating.

In a crystal that is diffracting X-rays the atoms, as diffracting centers, are arranged regularly in three dimensions. If these atoms lie at the corners of unit cells of a cubic crystal — that is, at the points of a simple cubic lattice — the conditions for reinforcement of the diffracted rays will be similar to those for a single row of points. If in this simple case (Figure 66) δ_0, ϵ_0 and ζ_0 are the direction cosines of the incident ray and δ, ϵ and ζ are the corresponding ones for the diffracted beam, all measured with relation to right angled cartesian coördinates, the conditions for constructive interference of the rays M_pN_p are determined by the three equations

$$\left.\begin{aligned} a_0(\delta - \delta_0) &= h_0'\lambda \\ a_0(\epsilon - \epsilon_0) &= k_0'\lambda \\ a_0(\zeta - \zeta_0) &= l_0'\lambda \end{aligned}\right\} \quad \ldots \ldots \ldots \quad (12)$$

where k_0' and l_0', like h_0', are integers.

Transposing:

$$(\delta - \delta_0) = h_0'\lambda/a_0;\ (\epsilon - \epsilon_0) = k_0'\lambda/a_0;\ (\zeta - \zeta_0) = l_0'\lambda/a_0.$$

Squaring these and adding together

$$\delta^2 - 2\delta\delta_0 + \delta_0^2 + \epsilon^2 - 2\epsilon\epsilon_0 + \epsilon_0^2 + \zeta^2 - 2\zeta\zeta_0 + \zeta_0^2 = \frac{\lambda^2}{a_0^2}(h_0'^2 + k_0'^2 + l_0'^2).$$

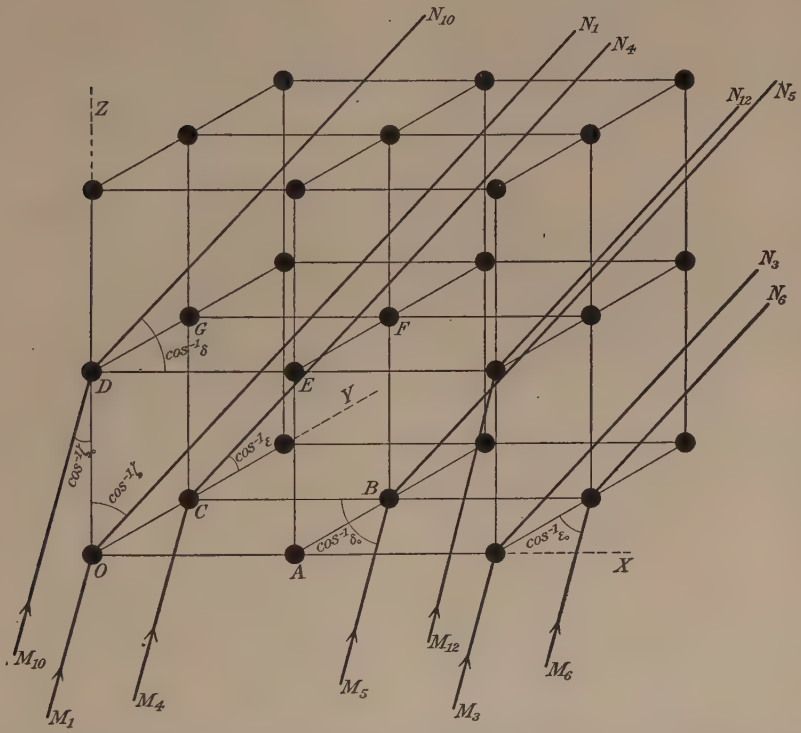


FIG. 66.—The diffraction relations of the rays M_pN_p for a simple cubic arrangement of diffracting centers. The cube OABCDEFG is the unit.

But since the sum of the squares of the direction cosines of a line is equal to unity,

$$2 - 2(\delta\delta_0 + \epsilon\epsilon_0 + \zeta\zeta_0) = \frac{\lambda^2}{a_0^2}(h_0'^2 + k_0'^2 + l_0'^2).$$

The angle of deviation 2θ, that is, the angle between the incident and the diffracted ray (Figure 67), is given by the usual relation

$$\cos 2\theta = \delta\delta_0 + \epsilon\epsilon_0 + \zeta\zeta_0$$

so that

$$2 - 2\cos 2\theta = \frac{\lambda^2}{a_0^2}(h_0'^2 + k_0'^2 + l_0'^2) = 4\sin^2\theta$$

or

$$\lambda = \frac{2a_0}{\sqrt{h_0'^2 + k_0'^2 + l_0'^2}} \sin\theta.$$

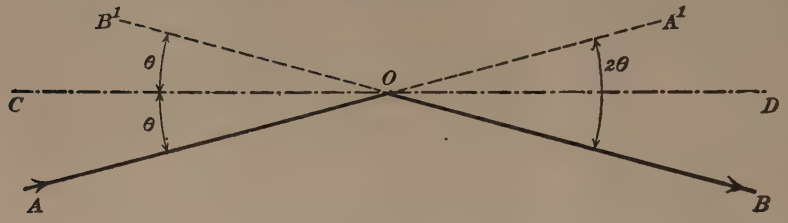


FIG. 67.—If AO is an incident and OB a diffracted beam, $A^1OB = 2\theta$ is the angle of deviation and CD is the trace of the "reflecting" plane.

If $h_0' = nh_0$, $k_0' = nk_0$ and $l_0' = nl_0$ where n is the highest common divisor of h_0', k_0' and l_0', then

$$n\lambda = \frac{2a_0}{\sqrt{h_0^2 + k_0^2 + l_0^2}} \sin\theta. \quad . \quad . \quad . \quad . \quad (13a)$$

If the analogous expression is deduced for groupings of unit cells which possess other than cubic symmetry, they are found to have a corresponding form:

$$n\lambda = \frac{2a_0}{\sqrt{F(h_0, k_0, l_0; abc; \alpha\beta\gamma)}} \sin\theta \quad . \quad . \quad . \quad . \quad (13b)$$

where $F(h_0, k_0, l_0; abc; \alpha\beta\gamma)$ is a quantity involving second degree terms in h_0, k_0 and l_0 and the crystallographic constants — the axial ratio and axial angles.

A possible geometrical interpretation of this equation, particularly of the terms involving the integers h_0, k_0 and l_0 is suggested by the following considerations. As an ideal case are to be imagined two, or more, infinitely thin sheets of plane transparent material parallel to one another and separated by a distance d (Figure 68).[1] If a beam of light AO strikes the sheets at the angle θ, some will be reflected along the line OB. Of the remainder, some will be reflected along O^1B^1, the rest being transmitted at O^1, and this process repeated for other sheets which may be present. The difference in path between the ray AOB and the ray AO^1B^1 is

[1] Though this experimental arrangement can scarcely be realized with ordinary light a similar phenomenon is exhibited in the color effects of thin films. In this case the interference takes place between beams reflected, not from different films, but from opposite faces of a single film.

$$OO^1 - OC = \frac{d}{\sin\theta} - \frac{d\cos 2\theta}{\sin\theta} = \frac{d}{\sin\theta}(1 - \cos 2\theta) = 2d\sin\theta.$$

When this path difference equals half of one wave length, or some odd integral multiple thereof, the two beams AOB and AO^1B^1 will be exactly

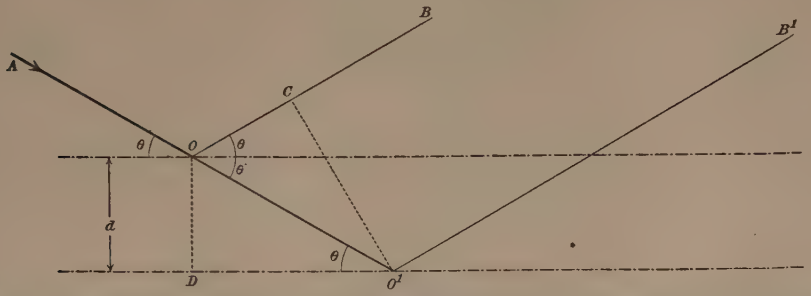


FIG. 68.—The phase relationships of reflections from a pile of infinitely thin reflecting plates.

out of phase and capable of destructive interference. When, on the other hand, 2d sin θ is some number of whole wave lengths, then the two beams will reinforce each other. Between these two extremes there will be a partial interference of the rays. Thus the light reflected from the two sheets of material will range in intensity continuously between zero and a maximum. If the number of sheets is increased, the interference would

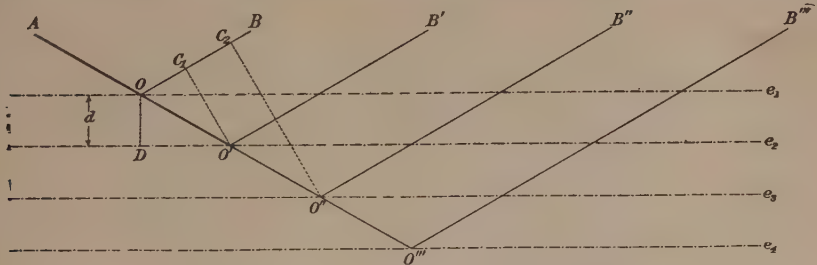


FIG. 69.—In this figure the path differences

$AO'B' - AOB = OO' - OC_1 = \frac{1}{4}\lambda.$
$AO''B'' - AOB = OO'' - OC_2 = 2OO' - 2OC_1 = 2(OO' - OC_1) = \frac{1}{2}\lambda.$

always remain constructive for the maxima and completely destructive for the minimal positions of half wave length differences in phase, but for the intermediate region the destructive interference will become more and more complete the greater the number of the sheets until eventually the reflection pattern will consist merely of a succession of bright beams separated by regions of total darkness. That this will be true may be

seen from a consideration of the intensity of reflection in the simple case shown in Figure 69. It is assumed in this figure that the path difference of the rays reflected by the first two sheets is a quarter of a wave length. With only two sheets in the pile the reflected beam would have a medium intensity resulting from the compounding of the two rays one fourth a wave apart. If a third reflecting plate is added, its reflected ray AO″B″ will be exactly opposite in phase to AOB and the resulting reflection will be diminished through a destruction of an amount of AOB equivalent to the amplitude of AO″B″; it will be still further lessened by the addition of a fourth sheet which will reflect AO‴B‴ exactly out of phase with AO′B′. By the same procedure it is clear that as more plates are added the destructive interference will become increasingly effective and thus the intensity of reflection will approach closer and closer to zero. With enough plates in the pile, the same destructive interference obviously would take place with any fractional path difference between AOB and AO′B′. Consequently the intensity maxima from such a large pile of plates have positions defined by the expression

$$n\lambda = 2d \sin \theta \qquad . \; . \; . \; . \; . \; . \qquad (13c)$$

where n is an integer. This expression has the same form as the equation (13a) which gives the positions of intensity maxima for X-rays diffracted by a simple cubic distribution of diffracting points. Since an infinite number of parallel planes can be passed through the points of such a grouping, this similarity suggests that it might prove convenient to consider the diffraction of such a regular arrangement of points as *geometrically* equivalent to reflection in a series of equidistant parallel planes.

The question of whether a plane of diffracting points would send back a beam of X-rays incident upon it which would obey the law of ordinary reflection is readily answered in the affirmative. In Figure 70 if A_1C is the wave front of a beam incident upon a row of points A_1, A_2, A_3 . . . A_p capable of acting as diffracting centers, the usual Huygens construction immediately shows that a reflected ray will have the wave front A_8D so situated that the angle θ_1 is equal to the angle θ_2.

If the analogy [1] between the reflecting sheets and the diffraction of X-rays by spacially distributed points is to be pressed, the quantity $a_0/\sqrt{F(h_0, k_0, l_0, abc; \alpha\beta\gamma)}$ of (13b) must be interpreted in terms of the distance between reflecting planes of points. In a regular latticework of points such as that formed by the corners of an extended repetition of the unit cells of a space grouping (Figure 47 for example) it is always possible to pass a series of planes which will be parallel to one another

[1] The explanation of X-ray diffraction effects in terms of reflections from atomic planes was given by W. L. Bragg, Proc. Camb. Phil. Soc. *17*, 43 (1913).

and contain all of the points of the lattice. The planes of such a series will be separated by a constant interval and, having integral indices, will be parallel to some possible face of an analogous crystal.

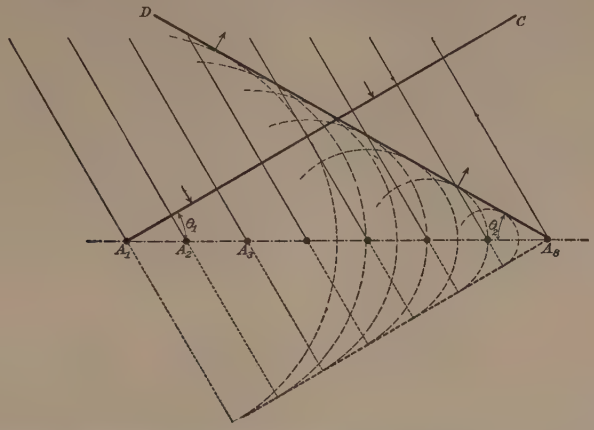


FIG. 70.—Huygens construction to show that a wave front A_1C will be "reflected" as DA_8 by the regularly spaced diffracting points A_1–A_p.

The distance between two neighboring planes of such a series (Figure 71) can be calculated as follows.[1] According to equation (1) of Chapter I

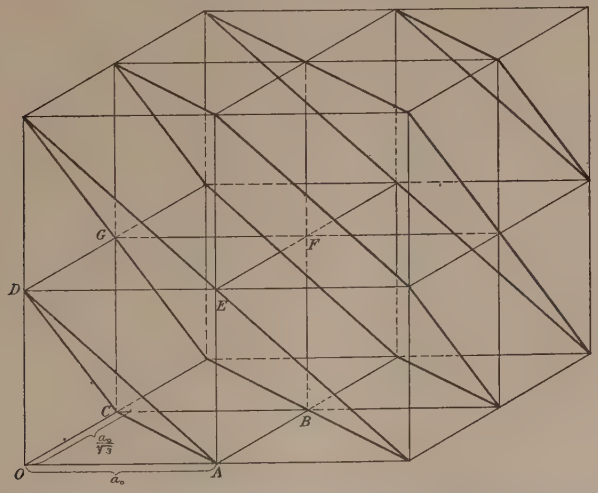


FIG. 71.—The succession of (111) planes in a simple cubic arrangement of points. The cube OABCDEFG is the unit.

[1] A deduction of interplanar distance resembling the one used here was made several years ago (but never published) by J. H. Ellis. In a slightly different form its results are given by A. W. Hull, Phys. Rev. *10*, 661 (1917).

the equation for a plane having the indices (hkl) referred to cubic axes is

$$hx' + ky' + lz' - D = 0.$$

The distance of this plane from the origin is

$$\frac{D}{\sqrt{h^2 + k^2 + l^2}}.$$

Since a parallel plane passing through the lattice point $P(x_1', y_1', z_1')$ has the equation

$$hx' + ky' + lz' - (hx_1' + ky_1' + lz_1') = 0,$$

the distance of this second plane from the first will be the difference of their distances from the origin, or

$$\frac{hx_1' + ky_1' + lz_1' - D}{\sqrt{h^2 + k^2 + l^2}}.$$

Similarly the distance of the parallel plane through $P(x_2', y_2', z_2')$ from the original plane is

$$\frac{hx_2' + ky_2' + lz_2' - D}{\sqrt{h^2 + k^2 + l^2}}$$

and their distance apart is

$$\frac{h(x_1' - x_2') + k(y_1' - y_2') + l(z_1' - z_2')}{\sqrt{h^2 + k^2 + l^2}} \quad . \ . \ . \ . \quad (14a)$$

From the nature of the cubic lattice $x' = pa_0$, $y' = qa_0$, $z' = ra_0$ so that (14a) becomes

$$\frac{[h(p_1 - p_2) + k(q_1 - q_2) + l(r_1 - r_2)]a_0}{\sqrt{h^2 + k^2 + l^2}} \quad . \ . \ . \ . \quad (14b)$$

where both h, k and l and p, q and r are integers. Thus the coefficient of a_0 in the numerator will always be a whole number and the minimal separation between like planes having the indices (hkl) and containing points of the lattice will be given by (14b) when this coefficient assumes its lowest possible value. It can be shown that if h, k and l are any three integers it is always possible to pick three other integers e, f and g so that

$$he + kf + lg = 1.$$

Since in an indefinitely extended lattice p, q and r may have any integral values desired, it follows that for a grouping of points at the corners of unit cubes

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \quad . \ . \ . \ . \quad (15a)$$

where d_{hkl} is the smallest distance between like planes with the indices (hkl).

From this identity in form between the expressions (a) for the diffraction of X-rays by regularly arranged diffracting centers in space and (b) for the reflection by uniformly spaced planes of diffracting centers, the fundamental likeness of these two *geometrical* ways of viewing X-ray diffraction phenomena is established. The outstanding value of the reflection point of view probably lies in its ability to attach a readily pictured and usable significance to the phase numbers h_0, k_0 and l_0 of expressions (13). This usefulness is particularly great in the treatment of diffraction effects from definitely oriented crystals since it employs the same terms (the indices) required to describe the crystal setting. In view of the widespread application which has accompanied the development of this reflection idea, the fact that it is essentially an artifice must be clearly understood. As a geometrical analogy it may correctly be used, but as long as X-rays are treated as wave motions their diffraction effects must be imagined as actually arising from the mutual interference of rays diffracted by spacially distributed scattering centers. As a consequence any discussion which aims to reproduce (as nearly as possible) the physical mechanism of X-ray diffraction cannot proceed from this reflection standpoint.

The diffraction numbers h_0, k_0 and l_0 and the indices of sets of reflecting planes (hkl) are the same for extended groupings composed of an association of the unit cells of each of the other systems of symmetry. This correspondence can be shown by a procedure similar to the foregoing one. It is thus permissible to write

$$n\lambda = 2d_{hkl} \sin \theta_n = \frac{2a_0}{\sqrt{F(hkl;\ abc;\ \alpha\beta\gamma)}} \sin \theta_n \quad . \ . \ . \ . \quad (16)$$

as the expression governing the possible positions of effects from assemblages of diffracting centers arranged at the corners of unit cells having crystallographic symmetry.

It has now been shown that for groupings built up from unit cubes expressions (15) and (16) have the form

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \quad . \ . \ . \ . \ . \quad (15a)$$

$$n\lambda = \frac{2a_0}{\sqrt{h^2 + k^2 + l^2}} \sin \theta_n \quad . \ . \ . \ . \ . \quad (16a)$$

For those composed of unit cells of each of the other systems of symmetry,[1] equations (15) and (16) will take the following forms:

[1] These equations (15) in a slightly different form are given by A. W. Hull, Phys. Rev. *10*, 661 (1917).

For the tetragonal unit cell: $a : b : c = 1 : 1 : c$ and $\alpha = \beta = \gamma = 90°$,

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + (l/c)^2}} \quad . \quad . \quad . \quad . \quad . \quad (15b)$$

and

$$n\lambda = \frac{2a_0}{\sqrt{h^2 + k^2 + (l/c)^2}} \sin \theta_n \quad . \quad . \quad . \quad . \quad . \quad (16b)$$

For the orthorhombic unit: $a : b : c = a : b : 1$ and[1] $\alpha = \beta = \gamma = 90°$,

$$d_{hkl} = \frac{c_0}{\sqrt{(h/a)^2 + (k/b)^2 + l^2}} \quad . \quad . \quad . \quad . \quad (15c)$$

and

$$n\lambda = \frac{2c_0}{\sqrt{(h/a)^2 + (k/b)^2 + l^2}} \sin \theta_n \quad . \quad . \quad . \quad . \quad (16c)$$

For the hexagonal unit: $a : b : c = 1 : 1 : c$ and $\alpha = \beta = 90°$, $\gamma = 120°$,

$$d_{hkl} = \frac{a_0}{\sqrt{4/3(h^2 + hk + k^2) + (l/c)^2}} \quad . \quad . \quad . \quad . \quad (15d)$$

and

$$n\lambda = \frac{2a_0}{\sqrt{4/3(h^2 + hk + k^2) + (l/c)^2}} \sin \theta_n \quad . \quad . \quad . \quad . \quad (16d)$$

For the rhombohedral unit: $a : b : c = 1 : 1 : 1$ and $\alpha = \beta = \gamma \neq 90°$,

$$d_{hkl} = \frac{a_0\sqrt{1 + 2\cos^3\alpha - 3\cos^2\alpha}}{\sqrt{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + hl + kl)(\cos^2\alpha - \cos\alpha)}} \quad (15e)$$

and

$$n\lambda = \frac{2a_0\sqrt{1 + 2\cos^3\alpha - 3\cos^2\alpha}}{\sqrt{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + hl + kl)(\cos^2\alpha - \cos\alpha)}} \sin \theta_n \quad . \quad . \quad (16e)$$

For the monoclinic unit: $a : b : c = a : b : 1$ and $\alpha = \beta = 90°$, $\gamma \neq 90°$,

$$d_{hkl} = \frac{c_0}{\sqrt{\dfrac{(h/a)^2 + (k/b)^2 - \dfrac{2hk}{ab}\cos\gamma}{\sin^2\gamma} + l^2}} \quad . \quad . \quad . \quad (15f)$$

and

$$n\lambda = \frac{2c_0}{\sqrt{\dfrac{(h/a)^2 + (k/b)^2 - \dfrac{2hk}{ab}\cos\gamma}{\sin^2\gamma} + l^2}} \sin \theta_n \quad . \quad . \quad (16f)$$

[1] This form of the axial ratio arises from the fact that in crystallographic description the Y(b) rather than the Z(c) axis is usually taken as the principal axis. This applies also to the description of monoclinic crystals (see page 55).

For the triclinic unit: $a : b : c = a : 1 : c$ and $\alpha \neq \beta \neq \gamma \neq 90°$,

(15g)

$$d_{hkl} = \frac{b_0}{\sqrt{\begin{vmatrix} h/a & \cos\gamma & \cos\beta \\ k & 1 & \cos\alpha \\ l/c & \cos\alpha & 1 \end{vmatrix} + k \begin{vmatrix} 1 & h/a & \cos\beta \\ \cos\gamma & k & \cos\alpha \\ \cos\beta & l/c & 1 \end{vmatrix} + l/c \begin{vmatrix} 1 & \cos\gamma & h/a \\ \cos\gamma & 1 & k \\ \cos\beta & \cos\alpha & l/c \end{vmatrix}}{\begin{vmatrix} 1 & \cos\gamma & \cos\beta \\ \cos\gamma & 1 & \cos\alpha \\ \cos\beta & \cos\alpha & 1 \end{vmatrix}}}$$

and

(16g)

$$n\lambda = \frac{2b_0}{\sqrt{\begin{vmatrix} h/a & \cos\gamma & \cos\beta \\ k & 1 & \cos\alpha \\ l/c & \cos\alpha & 1 \end{vmatrix} + k \begin{vmatrix} 1 & h/a & \cos\beta \\ \cos\gamma & k & \cos\alpha \\ \cos\beta & l/c & 1 \end{vmatrix} + l/c \begin{vmatrix} 1 & \cos\gamma & h/a \\ \cos\gamma & 1 & k \\ \cos\beta & \cos\alpha & l/c \end{vmatrix}}{\begin{vmatrix} 1 & \cos\gamma & \cos\beta \\ \cos\gamma & 1 & \cos\alpha \\ \cos\beta & \cos\alpha & 1 \end{vmatrix}}} \sin\theta_n$$

Since one of the seven types of unit cells is fundamental to every possible crystal, equation (15) gives the separation between geometrically like planes within any crystal. A knowledge of these expressions (15) and (16) solves completely the problem of the positions of diffraction effects from any space assemblage of diffracting points which possesses crystallographic symmetry. With their aid the angle through which X-rays incident from any direction upon a crystal will be bent can be predicted as long as the atoms (or other diffracting centers) can be considered to be regularly arranged in space in conformity with the crystalline symmetry. It perhaps should be emphasized, as these equations indicate, that the positions of X-ray diffractions are in no way dependent upon the particular manner of distribution of the atoms within a crystal but only upon the crystallographic characteristics (the axial angles and axial ratio) and the absolute dimensions of the unit cell. In other words all cubic crystals which have unit cells of the same size, no matter what their chemical compositions and atomic (or electronic) distributions may be, will give diffraction effects in identically the same positions. The same would be true of course of two crystals of any other symmetry which had unit cells of equal size and shape.

The Intensity of X-ray Diffraction Effects from Crystals

Problems of atomic arrangement in crystals consequently must concern themselves rather with the other characteristic of diffraction effects — their intensities. From the standpoint of these problems it is unfortunate

that such intensity relations, either absolute or relative, cannot now be evaluated with even an approach to the completeness which marks the ability to predict diffraction positions. They can be expressed more simply and conveniently, and at least in the present stage of our knowledge as accurately, by following the reflection analogy.

The difficulties of the problem are both experimental and theoretical. Some of the complications [1] that are encountered when an attempt is made to obtain accurate intensity measurements will be mentioned when the various methods of observing diffraction effects are discussed in later chapters. Several efforts [2] have been made to obtain theoretically sound intensity expressions. They do not, however, give results in even approximate accord with experiment unless terms are introduced which are dependent upon the electronic arrangement within atoms. At the present time too little is known of the structures of atoms to permit an evaluation of these terms. For this reason theoretically sound equations cannot now be used in the determination of the structures of crystals.

It is therefore necessary to fall back for the present upon the use of empirical factors. These are two in number.[3] One describes the dependence of intensity upon the character of the scattering atoms, the other expresses its variation with the angle of deviation. By making the assumption that the amplitude of X-rays scattered by heavy atoms in the production of regular diffraction effects is greater than that of lighter atoms by an amount which is probably roughly proportional to the atomic number, it is possible to deduce the structures of such simple crystals as the alkali halides. A further study of the intensity of reflection from planes in these crystals shows in a general way how the intensity of reflection varies with the angle of deviation and also the extent to which a proportionality between amplitude and atomic number is fulfilled.[4] From the fact that the intensity of reflection is related to the internal structure of the scattering atoms it is scarcely to be anticipated that quantitatively applicable laws can be found. Nevertheless the following working rules are approximately fulfilled for moderate angles of reflection and, if their limitations are held clearly in mind, they may safely be employed in the determination of crystal structure. It is essential, however, that their very qualitative character be emphasized because in the past a literal acceptance has been a most fruitful source of error.

The assumption that scattering power follows approximately the atomic

[1] See especially W. L. Bragg, R. W. James and C. H. Bosanquet, Phil. Mag. *41*, 309 (1921); *42*, 1 (1921).

[2] C. G. Darwin, Phil. Mag. *27*, 315, 675 (1914). A. H. Compton, Phys. Rev. *9*, 29 (1917). A. H. Compton, Bull. Nat. Research Council *4*, No. 20, p. 12 (1922). See also M. Laue, op. cit.

[3] W. L. Bragg, Proc. Roy. Soc. A. *89*, 468 (1914).

[4] These factors were not originally deduced in this fashion.

number of the scattering atoms is in agreement both with earlier knowledge and with crystal structure data. Existing information suggests that the amount of X-rays of ordinary wave lengths scattered by an atom will depend upon both the number and the positions of the electrons surrounding its nucleus. Since the number of these electrons parallels the atomic numbers of the elements it is to be expected that the scattering power of an atom for such X-rays will be greater for heavy than for light atoms. The amount of radiation scattered by an atom will depend upon the interference which occurs between rays sent out by its electrons and this in turn will be a function of its electronic configuration. If the distance between these electrons were small compared with the wave length of the scattered X-rays, their intra-atomic interference would be negligible and there would be a linear proportionality between scattering power and atomic number. Some early measurements [1] have indicated a simple proportionality between atomic number and the *amplitude* of reflected X-rays: thus in calcium fluoride two fluoride ions (N = 10) are closely equivalent in reflecting power to one calcium ion (N = 18); or in potassium chloride no difference can be distinguished between the scattering of a potassium ion (N = 18) and a chloride ion (N = 18). But in the isomorphous sodium fluoride, though sodium ions and fluorine ions have the same number of electrons (N = 10) a difference can be detected in their scattering powers. Furthermore many crystal structure data show that the heavier elements scatter appreciably more, electron for electron, than do atoms of low atomic weight. As a consequence it is not legitimate in crystal analysis to make more than a qualitative application of this proportionality between amplitude and atomic number. Whenever feasible, it is best to limit intensity comparisons to planes composed of only one kind of atom.

It has been seen that when they are located only at the corners of unit prisms, the atomic diffracting centers in a crystalline structure will lie in a series of equally spaced planes parallel to any possible crystal face (hkl). The intensity of X-ray reflection from (hkl) in such a simple atomic grouping, and in more involved ones after they have been corrected for their more complicated structures, has been found to fall off rapidly with increase in the angle of reflection, or what amounts to the same thing, decrease in the spacing of like planes. It was early suggested [2] that measurements of intensity from single faces of crystals show that for this simple atomic array the intensities of reflection for the first, second, third, etc. orders stand in the ratio of

$$100 : 20 : 7 : 3 : 1 : \text{etc.}$$

[1] W. L. Bragg, Proc. Roy. Soc. A. *89*, 468 (1914).
[2] *Ibid.*

One of the known factors entering into this decrease in intensity with increase in the angle of reflection is the thermal agitation of the atoms about equilibrium positions.[1] If this ratio, or "normal decline," is corrected as well as possible for the temperature effect, and for the polarization factor $\frac{1}{2}(1 + \cos^2 2\theta)$ of expression (10) of Chapter II, the intensity of reflection appears to be roughly proportional to the square[2] of the spacing between like reflecting planes, that is, to $(d_{hkl}/n)^2$. The "normal decline" itself is very approximately expressed by $(d_{hkl}/n)^{2.35}$.

An expression of the form $(d_{hkl}/n)^2$ is not to be expected from any known theoretical considerations. The crystal structure data now available show acceptable agreement with it in the reflections from the simpler planes of many crystals. At the same time they seem to show a much greater decrease in intensity with increased angle of deviation for large angles; hence the correspondence is not good where planes with complicated indices are concerned. Numerous examples of this are apparent in the existing crystal structure data and it seems probable that this simple expression is the result of the more or less chance operation of several other factors. These data make it clear (see for example the case of calcite) that it is scarcely allowable to make intensity comparisons between complicated planes unless they have similar spacings or unless planes with small spacings have greater intensities than those with larger spacings. Even in such instances there is no assurance that two complicated planes, corrected for structure and other extraneous effects, will give exactly the same intensities of reflections if their spacings are the same. In spite of these obvious insufficiencies of the "normal decline," so many intensity comparisons are possible if existing diffraction methods are used to their full possibilities that the structures of many crystals can be deduced with a great certainty of correctness.

In the light of the preceding discussion it will be seen that the best possible calculated approach to the observed intensity of reflection from a plane (hkl) of a simple unit cell array of atoms is offered by writing

$$I \propto \left(\frac{d_{hkl}}{n}\right)^2 \Phi \frac{1 + \cos^2 2\theta}{2} \sigma^2 = \left(\frac{d_{hkl}}{n}\right)^{2.35} \sigma^2 \quad . \quad . \quad . \quad (17)$$

where σ is the scattering power of the atoms composing the equidistant sets of planes parallel to (hkl) and Φ is a term expressing the effects due to thermal agitation.

In some powder photographs reflections have been obtained through angles for which $2\theta > 90°$. These large angle reflections seem to show

[1] P. Debye, Ann. d. Physik *43*, 49 (1914); Verhl. d. Deutsch. phys. Ges. *15*, 678 (1913).
[2] W. H. Bragg, Phil. Mag. *27*, 881 (1914).

(see page 300) that as 2θ approaches 180° the intensity of the diffraction effects *increases* again with angle. To agree with this fact another expression of the form

$$I \propto \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \sigma^2 = \frac{1 + \cos^2 2\theta}{\cos \theta} \left(\frac{d_{hkl}}{n}\right)^2 \sigma^2 \quad . \quad . \quad . \quad (18)$$

has been proposed.[1] For reflection angles θ greater than 45° this proportionality is undoubtedly better than the preceding one. This additional factor $\frac{1}{\cos \theta}$ has been proposed on several occasions;[2] but at present (18) like all intensity expressions is empirical. Most of the best data for crystal structure investigations involve angles 2θ less than a right angle and within this region expression (17) seems to be the better of the two forms. It consequently will be chiefly used in the subsequent calculations.

Other terms, which cannot be exactly evaluated at present, will also enter into these proportionalities. Notable among them is the absorption. The influence of absorption during reflection probably depends upon the degree of perfection of the crystal;[3] furthermore when X-rays are passing through a crystal at an angle of reflection without being completely absorbed, the energy which is reflected will cause the "apparent absorption coefficient" under these conditions to be different from the one usually measured.[4] The best methods available for circumventing the influence of these additional factors will be mentioned when each of the modes of experimentation are described in subsequent chapters.

In any other arrangement of atoms than the simple one that has been discussed one or more new sets of parallel planes, having the same relative spacings amongst themselves but lying somewhere between like planes of the original set, will be required to contain all of the atoms in a crystal. For example, in the simple cubic latticework of points geometrically like planes parallel to the (100) and (110) planes will have the relative spacings of b and c of Figure 72. In the very simple case of a cubic body-centered arrangement (Figure 73) it is evident that the additional points lying at the centers of the unit cubes will introduce a second set of atomic planes parallel to the (100) faces and midway between planes of the first set. No such new series appears parallel to (110) and the sequence of like planes in these two important directions becomes that of Figure 73, *b* and *c*.

The intensity of reflection from such series of planes depends upon both the amplitude and the phase of the reflections from each of them.

[1] J. M. Bijvoet, Thesis, University of Amsterdam, p. 38 (1923).
[2] For instance, J. M. Bijvoet, op. cit., p. 27.
[3] C. G. Darwin, op. cit.
[4] W. H. Bragg, op. cit.

This phase, or structure, factor will be of the general form:

$$I \propto \left[\sum_s \sigma F(\phi)\right]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where $F(\phi)$ expresses the phase relations of the reflection from each of the s sets of reflecting planes; σ, as before, is the scattering power of the

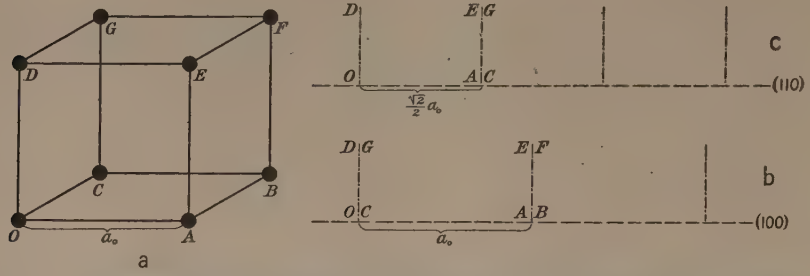


FIG. 72*a*. —The unit cell (OABCDEFG) of a simple cubic arrangement of points.
b. —The succession of (100) planes in this grouping.
c. —The succession of (110) planes in this grouping.

atoms composing these planes; and $\sum_s$ signifies that the effects from each set are to be summed.

Again taking the case of a cubic crystal as illustrative, the form [1] of this phase factor for a reflection (hkl) from any arrangement of atoms can be obtained as follows. In so doing the equivalent of the assumption that

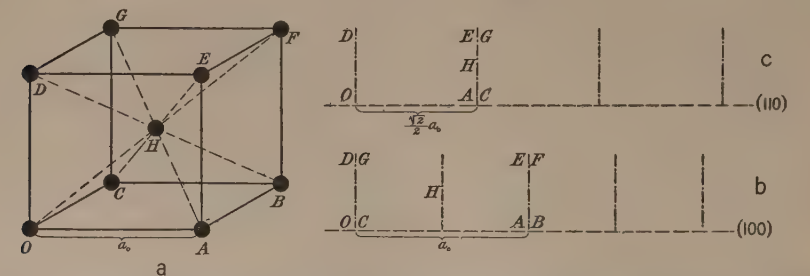


FIG. 73*a*. —The unit cell (OABCDEFG) of a body-centered cubic arrangement of points.
b. —The succession of (100) planes in this grouping.
c. —The succession of (110) planes in this grouping.

there is no phase lag during reflection will be made. The distribution of atomic planes parallel to (hkl) in any crystal can be represented as p, q, . . . s of Figure 74; the origin of coördinates lies in the plane o_1. The intensity of reflection from (hkl) is I, its amplitude R; the amplitude of

[1] This problem is essentially the old one of compounding wave motions having the same period but differing in amplitude and in phase. See for instance A. Schuster, The Theory of Optics, London, 1919, p. 8.

the reflection from the p planes is p, that from the q planes is q, that from the s planes is s. Then the resulting amplitude of reflection arises from the compounding of these p, q, . . s amplitudes, all of the same period (spacing) p_1p_2, q_1q_2, . . . s_1s_2 but differing in amplitude and in phase. The displacement x_p at any instant t due to the wave from the p planes is

$$x_p = p \cos \omega(t - \eta_p);$$

that due to an s plane is

$$x = s \cos \omega(t - \eta_s),$$

where $p_1p_2 = q_1q_2 = 2\pi/\omega$. Since all of these displacements are in a

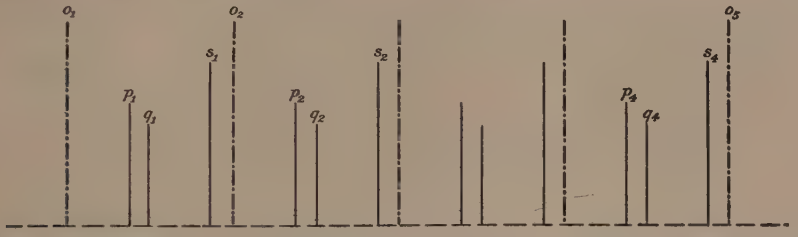


FIG. 74.—The sequence of planes (hkl) in some atomic arrangement. The plane o_1 contains the origin. The spacings $o_1o_2 = o_2o_3 = p_1p_2 = p_2p_3 = s_1s_2 =$ etc.

straight line and each produces its own effect, they may be combined algebraically so that

$$\begin{aligned} y \text{ (the total displacement)} &= x_p + x_q + \ldots + x_s \\ &= p \cos \omega(t - \eta_p) + q \cos \omega(t - \eta_q) + \ldots + s \cos \omega(t - \eta_s). \\ &= P \cos \omega t + Q \sin \omega t \end{aligned}$$

where

$$\left.\begin{aligned} P &= p \cos \omega\eta_p + q \cos \omega\eta_q + \ . \ . \ . \ \ s \cos \omega\eta_s \\ Q &= p \sin \omega\eta_p + q \sin \omega\eta_q + \ . \ . \ . \ \ s \sin \omega\eta_s \end{aligned}\right\} \quad . \ . \ . \ . \quad (19a)$$

Writing $P = R \cos \xi$ and $Q = R \sin \xi$,

$$\begin{aligned} y &= R(\cos \omega t \cos \xi + \sin \omega t \sin \xi) \\ &= R \cos (\omega t - \xi). \end{aligned}$$

From the form of this last equation it is clear that R is the amplitude of the wave compounded of those reflected from the planes p, q, . . . s. But since $P = R \cos \xi$ and $Q = R \sin \xi$,

$$R^2 = P^2 + Q^2 \propto I.$$

In the expression (19a) $\omega\eta_p$, $\omega\eta_q$ . . . $\omega\eta_s$ measure the phase of the reflections from the planes p, q, . . . s. If the difference in phase between the reflections from the planes o_1 and p_1 is ϕ_p, between o_1 and q_1 is ϕ_q

and between o_1 and s_1 is ϕ_s, then substituting these measures ϕ_s of the phase of the various reflections in (19a):

$$\left.\begin{aligned} P \propto A &= p\cos\phi_p + q\cos\phi_q + \ . \ . \ . \ s\cos\phi_s \\ Q \propto B &= p\sin\phi_p + q\sin\phi_q + \ . \ . \ . \ s\sin\phi_s \end{aligned}\right\} \ . \ . \ . \ . \ . \quad (19b)$$
$$\text{and } I \propto R^2 \propto A^2 + B^2.$$

If atoms were located at the corners of unit cells they would together place one atom within the unit and would form one set (o) of equally spaced reflecting planes (hkl). In the most general case, consequently, there may be as many of these sets of atomic planes as there are atoms in the unit of structure. The value of ϕ_s for each of these possible sets in terms of the coördinate positions of the atoms within the unit cube can be deduced as follows:

The shortest distance between geometrically like planes (hkl) in a cubic crystal is

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} = o_1o_2 = p_1p_2 = \ . \ . \ . \ = s_1s_2 \text{ (Figure 74)} \quad . \quad (15a).$$

The equation of such an (hkl) plane which contains the origin of coördinates is

$$hx' + ky' + lz' = (hx + ky + lz)a_0 = 0.$$

A parallel plane (hkl) through some point $x_sy_sz_s$ (as an atomic position within the unit cube) is similarly given by

$$\left[hx + ky + lz - \frac{(hx_s + ky_s + lz_s)}{\sqrt{h^2 + k^2 + l^2}}\right]a_0 = 0.$$

Its distance from the origin is

$$\frac{(hx_s + ky_s + lz_s)a_0}{\sqrt{h^2 + k^2 + l^2}} = o_1s_1 \text{ (Figure 74).}$$

Appreciable reflection has been shown to take place only when the waves reflected from adjacent geometrically like planes reinforce one another. Hence the difference in phase between the waves reflected by p_1 and by p_2, by p_2 and by p_3, by q_1 and by q_2, etc. will be $2\pi n$, and

$$\frac{\phi_s}{2\pi n} = \frac{o_1s_1}{o_1o_2} = \frac{o_1s_1}{s_1s_2} = \frac{\dfrac{(hx_s + ky_s + lz_s)a_0}{\sqrt{h^2 + k^2 + l^2}}}{\dfrac{a_0}{\sqrt{h^2 + k^2 + l^2}}} = hx_s + ky_s + lz_s$$

or

$$\phi_s = 2\pi n\,(hx_s + ky_s + lz_s).$$

Writing the scattering powers, σ_s, of the various atoms in place of p,q, . . . s and introducing the appropriate values of ϕ_s for atomic sets of planes corresponding to every atom within the unit cube, (19b) becomes

$$I \propto R^2 \propto A^2 + B^2,$$

$$A = \sigma_1 \cos 2\pi n\,(hx_1 + ky_1 + lz_1) + \sigma_2 \cos 2\pi n\,(hx_2 + ky_2 + lz_2) + \ldots + \sigma_s \cos 2\pi n\,(hx_s + ky_s + lz_s),$$

$$B = \sigma_1 \sin 2\pi n\,(hx_1 + ky_1 + lz_1) + \sigma_2 \sin 2\pi n\,(hx_2 + ky_2 + lz_2) + \ldots + \sigma_s \sin 2\pi n\,(hx_s + ky_s + lz_s) \quad . \quad . \quad . \quad (19c)$$

Thus it has been shown that for cubic crystals $\sum_s \sigma F(\phi_s)$ of (19) can be represented by (19c). The same form of expression holds for crystals having other symmetry properties.

Expression (19) may then be written (introducing $\bar{n}$ in place of σ) as:[1]

$$I \propto \left(\frac{d_{hkl}}{n}\right)^{2.35} \left\{ \begin{matrix} \left[\sum_s \bar{N}_s \cos 2\pi n\,(hx_s + ky_s + lz_s)\right]^2 + \\ \left[\sum_s \bar{N}_s \sin 2\pi n\,(hx_s + ky_s + lz_s)\right]^2 \end{matrix} \right\} =$$

$$\left(\frac{d_{hkl}}{n}\right)^{2.35} \times (A^2 + B^2) \quad . \quad . \quad . \quad . \quad (20),$$

where the summation is to be taken over every diffracting center (atom) within the unit cell.

Summary.—Two expressions have now been discussed. The first (16) permits the calculation of the positions of all possible diffraction effects from a crystal in terms of its symmetry characteristics, the spacing of like planes normal to some crystal face and the wave length of the X-rays. With the second (20) the relative intensities of reflection from any plane of any distribution of atoms in a crystalline arrangement can be estimated. It can thus be foretold for any specified atomic arrangement which of the reflections that are possible according to (16) will actually appear and to predict in a roughly qualitative manner their relative intensities.

It is now possible to make a definite statement of the chief postulates which underlie the subsequent treatment of X-ray diffraction phenomena for crystal structure determination. They are essentially as follows:

(1) X-rays behave as if they are light waves of short wave length which can be diffracted by the atoms (or more accurately their electrons) in crystals. The approximate length of these waves can be obtained by application of quantum principles.

(2) The two "laws" of scattering are approximately, but only approximately, fulfilled. The first of these states that scattering power follows

[1] The intensity proportionality in essentially this form was used by S. Nishikawa, Proc. Math. Phys. Soc. Tokyo *8*, 199 (1915). It was first stated by R. W. G. Wyckoff, Am. J. Sci. *50*, 317 (1920).

roughly the number of electrons in an atom; according to the second the intensity of diffraction falls off with increased angles of diffraction, at least until 2θ in the preceding equations reaches a right angle. As a working expression of these "laws" it is considered that the requirements of expression (17) must be qualitatively met; the lack of precise knowledge of scattering, however, makes it impossible to set definite limits to their permissible variation. The element of personal judgment which must consequently be often introduced makes this postulate at present the most unsatisfactory of those which must be used.

(3) The use of the theory of space groups in crystal analysis permits the search not only for a possible structure but for the only one possible in the light of the two preceding postulates concerning the properties of X-rays. To achieve such unique solutions through the application of space group theory it is assumed (1) that the atoms giving observable diffraction effects occupy equilibrium positions fixed by the symmetry of the crystal and (2) that the results of the theory of space groups define all of the equilibrium atomic positions possible for any crystal.

The substance of these three postulates and their justification have been touched upon in the course of these first three chapters. By combining them with the content of these chapters and with the actual results of space group theory it is possible to develop systematic and more or less generally applicable methods of crystal structure investigation. Before proceeding to outline the character of these methods, however, the next three chapters will be devoted to a discussion of the different experimental procedures now available for observing X-ray diffractions. This also will include a consideration of the nature of the information which each of them can furnish.

Chapter IV. The Production and Interpretation of Laue Photographs

The Preparation of Laue Photographs

Laue photographs of a substance which forms good crystals are easily made. A fine X-ray beam, defined by passage through pin-holes in two, or more, sheets of lead (S′ and S″ of Figure 75) will be diffracted by a thin section of crystal at C. The resulting slit images arranged in a more

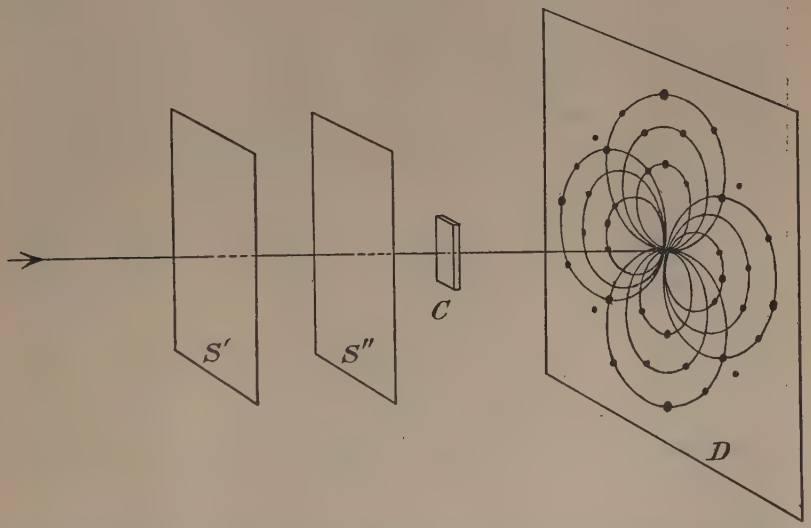


Fig. 75.—The Laue experiment. After passing through pin-holes in the lead sheets S′ and S″ the beam of X-rays strikes the crystal at C. The resulting diffraction pattern, as a series of pin-hole images, is registered on a photographic plate at D.

or less symmetrical fashion about the undeviated central image upon a photographic plate (D) constitute a Laue photograph. The symmetry of distribution of these spots is related to that of the crystal giving rise to them. This is clear, for instance, from the photographs of Figure 76; a four-fold pattern is obtained by passing the X-rays along four-fold axes of the cubic ammonium chloride, and three-fold patterns result when the X-rays travel parallel to the three-fold axes of quartz and of the cubic potash alum.

Apparatus.—Convenient dimensions for Laue photographic apparatus can be stated by reference to Figure 75. The lead slits (S′ and S″) may be from eight to ten centimeters apart and $\frac{1}{8}$ inch thick with pin-holes approximately 1.2 millimeters in diameter. The crystal section should

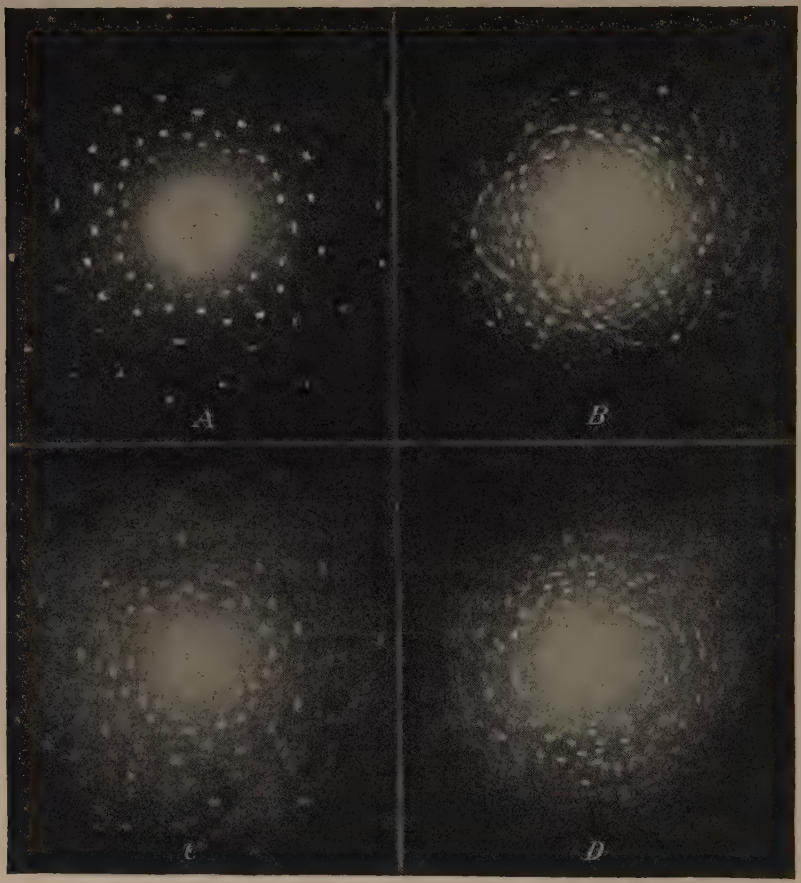


FIG. 76.—Laue photographs taken with X-rays passing along
a. The four-fold axis of a cubic crystal of ammonium chloride,
b. The three-fold axis of a cubic crystal of potash alum,
c. The three-fold axis of a hexagonal crystal of quartz,
d. A line normal to the cleavage face of orthorhombic barite.

if possible have an area large enough to cover the bundle of X-rays proceeding from the pin-holes. This, however, is not necessary: photographs suitable for crystal structure determinations have been prepared from crystals with a maximum dimension less than one millimeter. The thickness of the crystal will be anywhere from about one tenth of a millimeter

to one millimeter. The specimen should be thinner the higher the density and consequently the greater the absorbing power of the crystal for X-rays. If both the diffracting and the absorbing powers were adequately known it would of course be possible to calculate an optimum thickness for any crystal. This cannot, however, be done at the present time. The slip of crystal may be either pasted directly over the last lead slit or mounted upon some form of crystal holder. The first procedure is the simpler, the second has the advantage of allowing the crystal to be so mounted that both its orientation with respect to the X-ray beam and changes in this orientation for the preparation of additional photographs can be more precisely stated. Since the spots characteristic of Laue photographs are produced by X-ray beams proceeding from the irradiated crystal, the size of the Laue pattern will be proportional to the distance from the crystal to the photographic plate. For cubic crystals and others having an axial ratio not too greatly different from unity, this distance may conveniently be made equal to five centimeters. With other crystals a plate distance of four and occasionally of three centimeters will be found useful.

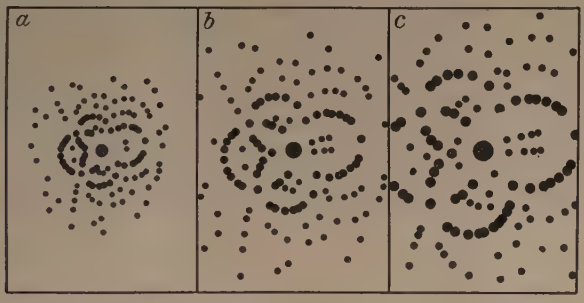


FIG. 77.—Tracings of three Laue photographs of calcite prepared with the X-rays striking normal to a (100) face. In the first the crystal-to-plate distance is 3 cm.; in the other two it is 5 and 7 cm. respectively. No attempt is made to reproduce the relative intensities of the diffraction spots.

The effect of variations in this distance upon the size of the resulting Laue photographs is illustrated by Figure 77.

A crude form of apparatus for the production of Laue photographs is shown in Figure 78. The body of this box is made of well-seasoned wood one inch thick, covered except in front with $\frac{1}{16}$ inch lead and provided with a cover also sheathed in thin lead. The front of the box is faced with the first of the two $\frac{3}{16}$ inch lead sheets which constitute the slits. The thin lead covering for the box is intended to shut off scattered and extraneous radiation and may be omitted if other X-ray equipment or radioactive material is not at hand to cause interference. The photographic plate used in this apparatus is 5 x 7 inches in size and should be

sealed in a black paper envelope during its exposure. In the instrument of Figure 78 the thin section of crystal is mounted upon a microscope cover glass with paraffin or balsam. The specimen holder is capable of motion in two directions at right angles to each other. The amount of this motion can be roughly measured upon the graduated circles c′ and c″.

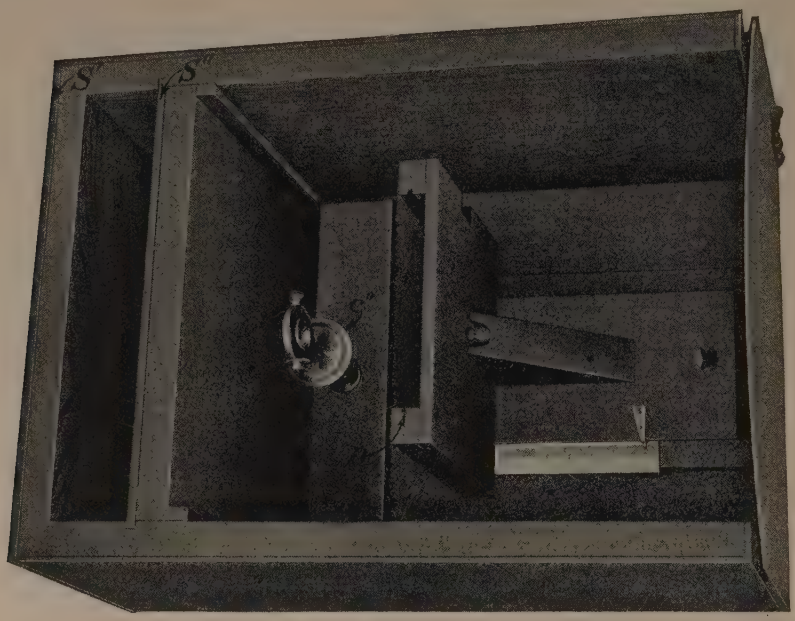


Fig. 78.—An early form of apparatus for the production of Laue photographs.

This early form of apparatus has been described primarily to show that only simple equipment is needed to make good Laue photographs.

The X-rays which produce Laue spots lie in the region of white radiation (Chapter II). It will be shown later that the most useful Laue photographs for the determination of the structures of crystals are prepared with a maximum tube potential of 50 to 60 kilovolts. Of the commercially available X-ray tubes one with a tungsten target is most satisfactory because it gives the greatest amount of continuous radiation. At this voltage an exposure of 15 milliampere-hours is usually sufficient to produce good Laue photographs. The length of exposure depends somewhat upon the thickness and size of the crystal specimen and largely upon its absorbing power. Laue photographs which exhibit a very large number of spots can be produced by operating the tube at a voltage higher than 60 kilovolts not only because the efficiency of production of white X-rays increases with impressed voltage but also because many more atomic

planes are in a position to reflect the shorter X-rays thus produced. Such high voltage Laue photographs can frequently be obtained with profit where only symmetry information is desired.

The grave injuries [1] to the health of the experimenter which result from exposure to X-rays require that care be taken in the shielding of X-ray tubes during the preparation of diffraction photographs. This protection must be more effective than that employed in the ordinary medical use of X-rays. Because of the long exposures required in obtaining crystalline diffraction, minute leaks which would be negligible over a period of some seconds may become of considerable importance after several hours. For these reasons all X-ray tubes used in crystal analysis should be enclosed in boxes covered with a thickness of lead sufficient to prevent the deterioration after several months of photographic plates placed outside the boxes.

There are several directions in which the Laue photographic apparatus of Figure 78 could profitably be improved. In the first place a more rigid construction would eliminate warping and a loss in alignment of the slit system over a period of time. This is accomplished by building the instrument entirely of metal using an appropriate casting as a base. For some purposes it would also be of advantage to have a more exact determination of the distance from the crystal to the photographic plate. An accuracy sufficient for ordinary purposes is directly attainable by meeting this requirement of greater rigidity. If it should be desired, still greater precision could probably be achieved by using the device of two photographic plates placed one behind the other at a carefully determined distance apart.[2] The method of finding the distance from crystal to plate by this procedure will be clear from Figure 79. The distances from the undeviated slit images O and O′ to corresponding points in the two photographs are OA and O′A′. From a measurement of these distances and an accurate knowledge of OO′ (the distance between the sensitive emulsions of the two photographic plates), CO (or CO′) can be obtained through the two similar triangles AOC and A′O′C:

$$\frac{CO}{OA} = \frac{CO'}{O'A'} = \frac{CO' - CO}{O'A' - OA} = \frac{OO'}{OA' - OA} \text{ and } CO = OA\,\frac{OO'}{OA' - OA}$$

[1] The physiological action of X-rays seems to be of at least two sorts. Exposure to a large quantity of X-rays will result in the well-known "burn," an inflamed condition of the skin which frequently develops into open sores, is extremely difficult to heal and is said sometimes to break out subsequently as a cancerous condition. Reasonable care will now prevent such "burns." Results seem to show, also, that a dosage of X-rays much less than that required to produce "burns" will, if frequently repeated, give rise to an anemia which in some instances has proved fatal. Little is now known of the minimal quantity of X-rays that is needed eventually to bring about this anemic condition.

[2] G. Wulff, Zeitsch. f. Kryst. *54*, 59 (1915).

This method might prove especially desirable in working with thick crystal specimens.

A third refinement would provide the apparatus with an instrument for accurately orienting the crystal with respect to the incident X-rays. Such a goniometric attachment is not now required for most work because

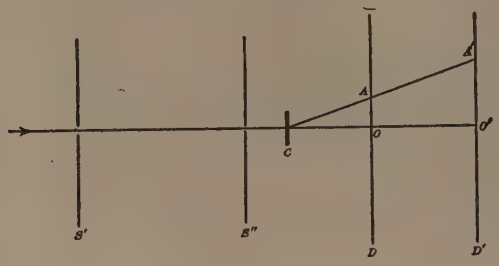


FIG. 79.

the exact orientation of the specimen can always be calculated from the Laue photograph itself if the approximate setting is known. It would, however, prove most useful in mounting small crystals for X-ray examination and, in some form or other, probably will be required for all observations after an increase in physical knowledge makes intensity comparisons from different planes more valuable. It would then frequently be necessary to obtain a Laue photographic reflection from some predetermined plane in a particular wave length by carefully setting the crystal.

When X-rays pass through the two pin-hole slits S′ and S″ of Figure 78, some will strike the edges of the second slit S″. The scattered radiation thus produced fogs somewhat the photographic plate. In making Laue

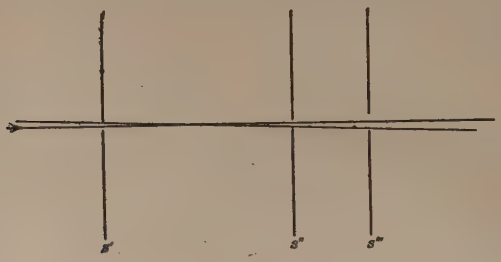


FIG. 80.

photographs through sections of good crystals, the diffracted radiation is so intense that this blackening is negligible. It may, however, quite overshadow the pattern from very small crystals. In this case a slit system must be used in which secondary rays from the slits have been eliminated. Such a series of pin-holes is shown in Figure 80. The size of the third slit,

S‴, which may if desired be made of some other metal than lead, is governed by the requirement that direct rays through S′ and S″ are not to be allowed to strike it at any point. The distance between S″ and S‴ must be great enough to shield the useful part of the plate. Better pin-holes can be made in gold than in lead. The greater density of the former also permits the use of a thinner slit. [If the metal is available it

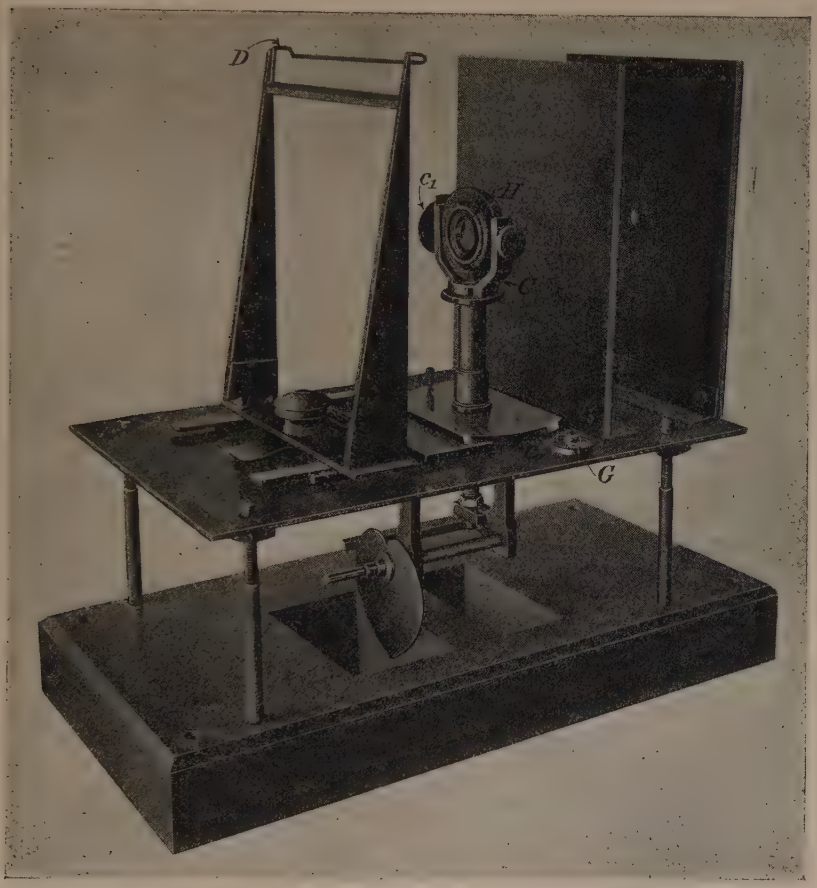


FIG. 81.—An improved form of apparatus for the production of Laue photographs.

is to be recommended that the parts of S′ and S″ through which the holes are drilled should be made of gold.

Various forms of Laue photographic apparatus have been made which incorporate one or more of these desirable, but for many purposes not strictly requisite, improvements. One is shown in Figure 81. Its essential parts are mounted upon a brass base. The crystal specimen held on

a microscope slide is mounted in a crystal holder (C) and centered with the aid of the removable template shown at G. Besides the motions (measured by c_1 and c_2) at right angles to one another which are possessed by the holder previously described, the collar (H) supporting the crystal can be rotated. This last motion is of particular advantage with strongly absorbing crystals because a series of unsymmetrical Laue photographs in slightly different orientations can be prepared by thus turning the crystal without largely altering the absorption in different parts of the photographs. The spectrographic apparatus to be described in the following chapter and shown in Figure 120 can equally well be used by substituting pin-holes for line slits and either mounting the crystal directly over the last of these slits or placing it in a goniometric crystal holder of the type just described. An instrument [1] has been built directly upon a Czapski two-circle goniometer; [2] another form [3] has been used to outline a possible procedure for determining symmetry properties of a crystal solely by the use of Laue photographs. An arrangement [4] whereby the position of the photographic plate rather than the diffracting crystal can be varied with respect to the incident X-ray beam has also been described.

The Preparation of Laue Photographs at other than Room Temperatures.— The study of Laue photographs both at elevated and at low temperatures will be of great value in following, for instance, the atomic rearrangements that are involved in many inversions. Very few results of X-ray diffraction measurements under such conditions have yet been made. Of these the only Laue photographs, besides some observations upon rolled metals,[5] are of sodium chloride at a temperature near 320°C and of boracite at 300°C, the temperature at which this mineral becomes isotropic. The furnaces used for these two latter measurements, both of which were carried out in the early days of X-ray diffraction investigations, have been described.[6]

The Interpretation of Laue Photographs

It has been shown that series of planes can be passed through the atoms of a crystal parallel to any imaginable face (hkl) and that the X-ray diffraction effects from a crystal can be conveniently interpreted as reflections from such series of parallel atomic planes. In accordance with equation (16) of Chapter III a beam of X-rays will be "reflected" by the (hkl) planes when

$$n\lambda = 2d_{hkl} \sin \theta_n$$

[1] G. Wulff, op. cit.
[2] S. Czapski, Zeitsch. f. Instrumentenkunde *13*, 1 (1893).
[3] R. Gross, Centr. Neues Jahrb. f. Mineral. 1920, p. 52.
[4] F. Rinne, Ber. K. Sächs. Ges. Wiss. Leipzig (Math.-phys. Klasse) *67*, 303 (1915).
[5] S. Nishikawa and G. Asahara, Phys. Rev. *15*, 38 (1920).
[6] M. Laue and J. S. van der Lingen, Physikal. Z. *15*, 75 (1914); H. Haga and F. M. Jaeger, Proc. Roy. Acad. Sci. Amsterdam *16*, 792 (1914).

An indefinitely large number of these series of planes can be imagined in the thin crystal sections used for making Laue photographs. They will be inclined at a large variety of different angles to the X-rays for any one crystal setting. Many of them then will meet the requirements of equation (16) for the reflection of some wave length present in the white X-radiation used. It is to be expected from this standpoint that a Laue experiment will yield a number of spots each capable of being considered a "reflection" from some possible crystal face (hkl). Since the inclination of the possible atomic planes is governed solely by symmetry, the distribution of spots upon the photographic plate will depend only upon the symmetry of the crystal and its orientation with respect to the X-ray beam. Thus all cubic crystals with X-rays traveling along four-fold axes give Laue spots at precisely the same positions. This would be equally true for any two similarly oriented crystals with identical axial ratios and angles.

Following the reflection analogy in the interpretation of Laue photographs it is necessary to identify the individual spots that occur with the planes which give rise to them. An integral multiple, $n\lambda$, of the wave length of the rays producing each spot can then be calculated from measurements upon the photograph. When the wave lengths of reflecting planes have been ascertained in this way intensity comparisons may be made to distinguish between the different structures otherwise found possible for the crystal under examination.

The Symmetry of Laue Photographs. Since diffraction effects can properly be considered as (internal) reflections from atomic planes parallel to a crystal face (hkl), there can be no difference between the results obtained from the face (hkl) or its parallel face ($\bar{h}\bar{k}\bar{l}$). The equivalence of reflections from (hkl) and ($\bar{h}\bar{k}\bar{l}$) means that in its diffraction effects every crystal will seem to have a center of symmetry. As a consequence the 32 classes of crystal symmetry reduce to 11 groups [1] when the symmetry of their X-ray phenomena is considered. The content of these groups is given in Table I. The symmetry of Laue photographs from crystals belonging to any class of symmetry can be deduced from the stereographic projections of the appropriate "master" classes of the second column. These projections are included amongst the figures of Chapter I.

The Determination of the Indices of the Planes Producing Laue Spots. The path of the X-rays producing a Laue spot can be shown diagrammatically in Figure 82. The incident beam OC and the ray CA reflected by a plane with the trace DB lie in the plane of the paper. The distance on the photographic plate between the spot caused by CA and the symmetrical undeviated slit image is AC′; CC′ is the distance from the crystal to the

[1] G. Friedel, Comptes rendus *157*, 1533 (1913).

TABLE I

(1) Crystallographic Symmetry	(2) Symmetry of X-ray Diffraction Effects
I. Triclinic System	
1C, 1Ci	1Ci
II. Monoclinic System	
2c, 2C, 2Ci	2Ci
III. Orthorhombic System	
2e, 2D, 2Di	2Di
IV. Tetragonal System	
4c, 4C, 4Ci	4Ci
4d, 4e, 4D, 4Di	4Di
V. Cubic System	
T, Ti	Ti
Te, O, Oi	Oi
VI. Hexagonal System	
A. Rhombohedral Division.	
3C, 3Ci	3 Ci
3e, 3D, 3Di	3Di
B. Hexagonal Division	
6c, 6C, 6Ci	6Ci
6d, 6e, 6D, 6Di	6Di

plate. By the reflection requirements the angle ACC′ is 2θ. The information in this figure combined with a knowledge of the distribution of the possible crystal faces (as reflecting planes) for any desired orientation permits the identification of Laue spots.

This problem of the distribution of possible reflecting planes is essentially the same that is met in ordinary crystallography when it is desired to represent the positions of various faces observed upon a crystal specimen and to determine the spacial relationships existing between them.

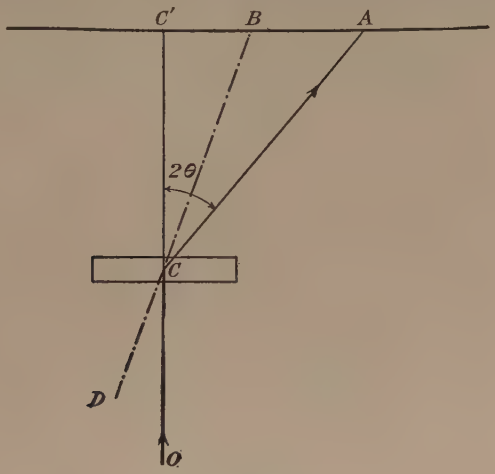


FIG. 82.

As such it has received a solution in numerous forms. Of these the most convenient and serviceable are the various kinds of graphical projection.

The symmetry of the crystal classes has been described in Chapter I with the aid of the stereographic projection. The first interpretation [1] of a Laue photograph in terms of the reflection analogy employed the following adaptation of this type of projection (Figure 83). A beam of X-rays is incident upon a crystal at C; those reflecting planes having the zone axis CO produce a set of reflections lying upon the surface of a circular cone with apex C and two generators AC and BC. For instance the ray reflected by the plane (through OC) which when extended to the photographic plate has the trace DOE will travel along the generator CF. The intersection of this circular cone with the sphere of projection is a circle of diameter C′F. The intersections of such circular cones with the plane of the photographic plate are ellipses. Their stereographic projections upon this plane are circles; thus the circle through C′ and G is the pro-

[1] W. L. Bragg, Proc. Roy. Soc. (London) *89A*, 246 (1913).

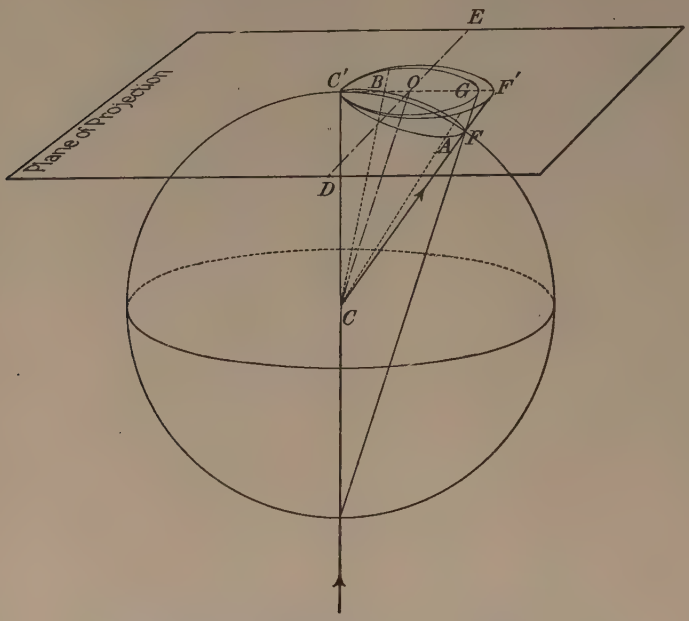


FIG. 83.—The stereographic projection of Laue spots.

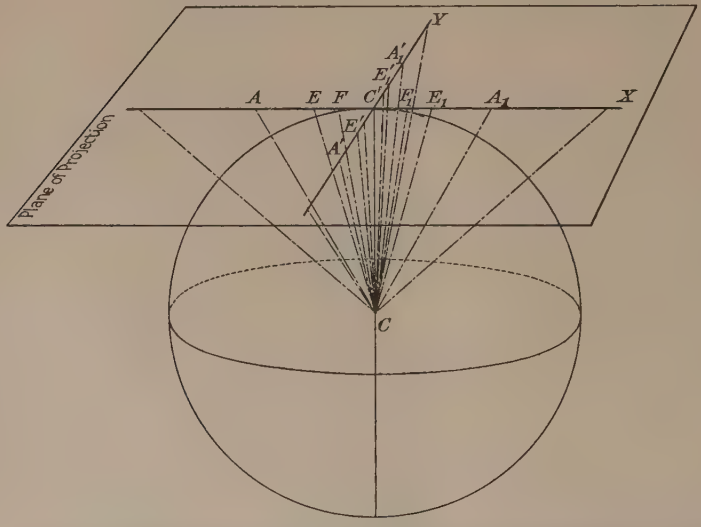


FIG. 84.—The intersections with the projection plane of zone axes useful in drawing the stereographic projection of Fig. 87.

jection corresponding to the ellipse passing through C′ and F′. The projections for the important zone ellipses give the projection of a Laue pattern. The Laue spots, as reflections from possible crystal faces, lie on the intersections of two ellipses. The indices of the spots (i.e., the indices of their reflecting planes) are given through the customary zone relationship (page 52) by the indices of the zone axes of their intersecting projection circles.

The method of preparing one of these projections can be illustrated by assigning indices to the simple Laue photograph obtained when X-rays travel along a four-fold axis of a cubic crystal of magnesium oxide (MgO). Figure 84 shows the intersections of some important zone axes with the plane of the photographic plate. The positions of these axes and the value of their indices will be clear from Figure 85 which is a section normal to

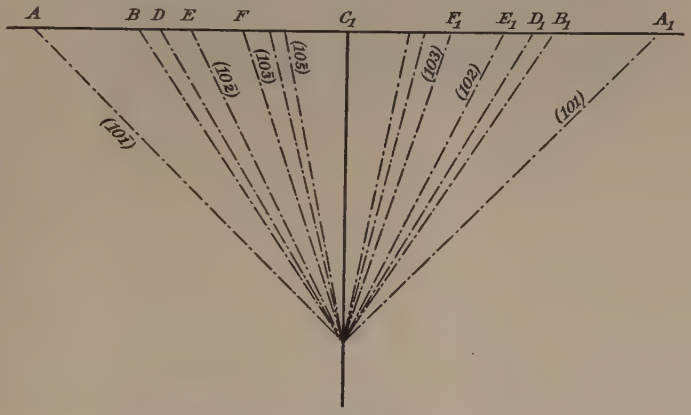


FIG. 85.—A section through the X and Z axes of Fig. 84 showing on this plane ACA_1 the zone axes necessary for drawing Fig. 87. A perpendicular section through $A'CA'_1$ would be exactly similar.

the plate and containing the Z- and the X- (or the Y-) axes of coördinates. The resulting projection of the Laue photograph of Figure 86 is shown in Figure 87. The distance (C′F′ of Figure 83) from the central undeviated image to a spot on a Laue photograph is related to the corresponding distance upon the projection (C′G) by the relation

$$f = \frac{4r^2g}{4r^2 - g^2}$$

where r is the radius (CC′) of the sphere of projection,
f is the distance (F′C′) of the spot upon the photograph and
g is its corresponding distance (GC′) upon the projection.

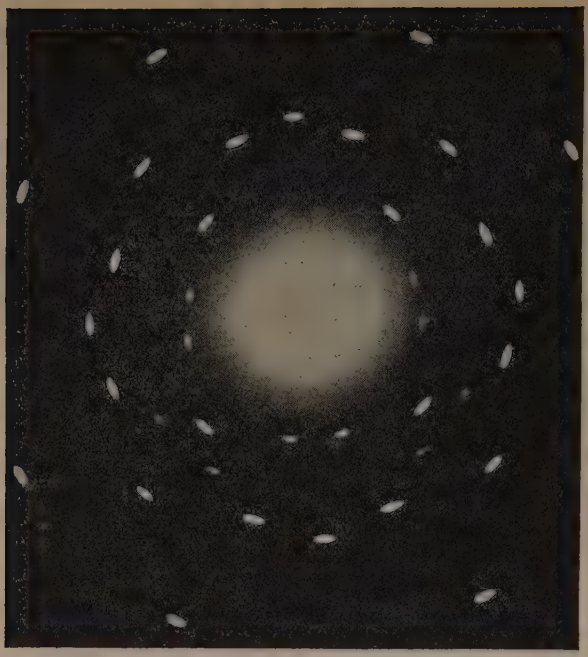


FIG. 86.—A Laue photograph of a cubic crystal of magnesium oxide. The incident beam of X-rays was parallel to a four-fold axis.

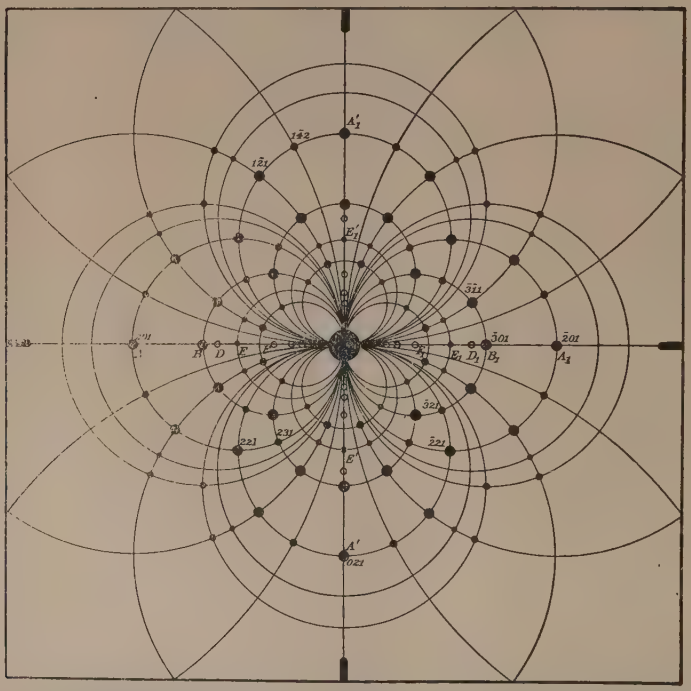


FIG. 87.—The stereographic projection of a Laue photograph of magnesium oxide taken with the X-rays passing along the Z-axis of coördinates. The intersections of the zone axes of Fig. 85 with the plane of projection are shown by open circles; the projections of Laue spots, as reflections of possible crystal planes, are marked by black circles. The size of these circles is roughly proportional to the intensity of their corresponding spots (Fig. 86).

Though this modified stereographic projection will furnish the indices of planes producing reflections in any Laue photograph, it is frequently difficult and time-consuming to make and must be carried out with considerable accuracy. As a consequence it has been replaced in crystal analysis by the simpler gnomonic projection.

The gnomonic projection [1] of a crystal located at the center (C) of the sphere of projection (Figure 88) is furnished by the intersections of the

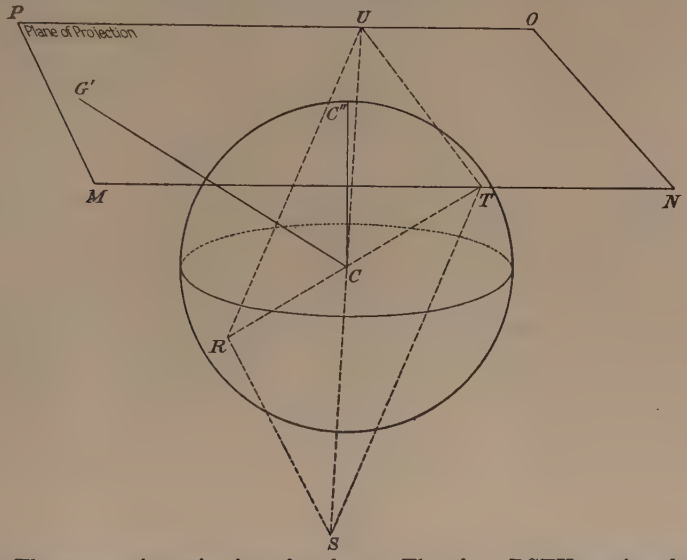


FIG. 88.—The gnomonic projection of a plane. The plane RSTU passing through the center C is parallel to some face of a crystal located at C. The line G'C is normal to RSTU. Its intersection with the plane of projection MNOP at G' is the gnomonic projection of the plane RSTU (and of its parallel crystal face).

normals to its faces with the tangent plane MNOP. Since all of the normals to the faces in a zone lie in one plane through the center of projection, their projected positions will all fall upon a straight line. This property is one of the outstanding advantages of the gnomonic projection. Its most desirable feature for the present purposes, however, lies in the fact that if the plane of projection is taken normal to one of the axes of reference, the indices of faces can be determined directly from the coordinates of their projected positions on this plane. A crystal so set that the Z, or c, axis is perpendicular to the plane of the projection, will be said to be in a "standard" orientation.

The gnomonic projection is readily adapted [2] to the analysis of Laue

[1] V. Goldschmidt, Über Projektion u. Krystallrechnung (1887); H. E. Boeke, Die gnomonische Projektion (Berlin, 1913).

[2] F. Rinne, op. cit.; R. W. G. Wyckoff, Am. J. Sci. *50*, 317 (1920).

photographs. In Figure 89 X-rays striking a crystal at C are reflected in a plane which produced is RSTU. The gnomonic projection of this plane upon MNOP, which is assumed to be the plane of both the projection and the photographic plate, is G′; its Laue spot will be registered at F. The lines G′C, CC″ and CF all lie in a plane and it is evident that if either the projection of a plane or the position of its Laue spot is known, the other can be calculated immediately. It is best to make all projections

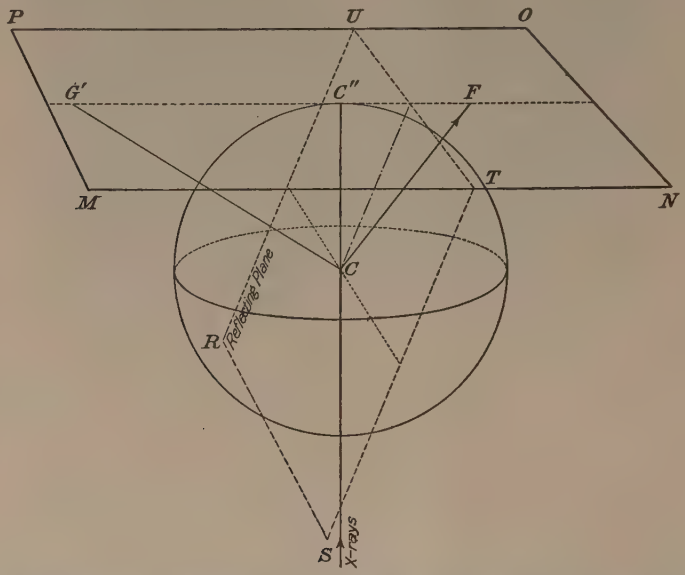


FIG. 89.—The gnomonic projection of a Laue spot. The X-rays incident at right angles to the plane of projection and of the photograph (MNOP) are reflected by a plane RSTU (when extended) in a crystal at C giving rise to a spot at F. By the gnomonic projection of the Laue spot F is to be understood the gnomonic projection of the reflecting plane RSTU. According to the preceding figure this point is G′.

with a constant radius (CC″) of five centimeters. Since Laue photographs are taken at various distances from the reflecting crystal, the plane of the projection will not always coincide with that of the plate. In such a case the relations between a Laue spot and its gnomonic projection can be expressed with the aid of Figure 90. In this figure the plane of the paper is perpendicular to both the plane MNOP and the plane RSTU of Figure 89. As before G′C′F is a straight line, FC′ is the distance of the spot from the central image and GC″ is the distance of the projected point from the center point of the projection. It then follows that

$$GC'' = CC'' \cot\theta = 5 \cot\theta \qquad \text{where}$$

$$\theta = \tfrac{1}{2} \tan^{-1} \frac{FC'}{CC'} \qquad . \quad . \quad . \quad . \quad (21)$$

In the ordinary crystallographic use of the gnomonic projection it is customary to describe the normal to a face by stating its longitude ϕ_1

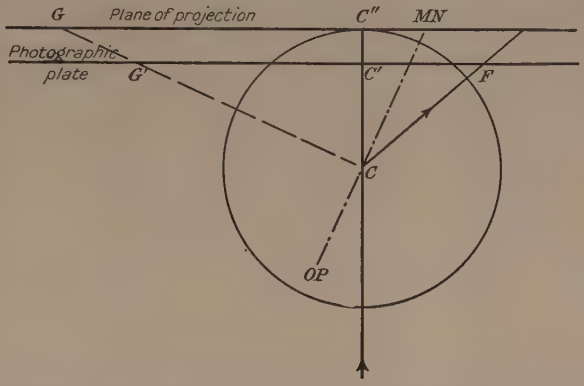


FIG. 90.—A section, G'CF, through the preceding figure showing the relations that exist if the plane of the photograph is not coincident with that of the projection.

(from an arbitrarily fixed zero position) and polar distance ρ_1 (Figure 91). These coördinates (ϕ_1, ρ_1) are the quantities that can be directly measured upon a crystal with the two-circle type of goniometer.

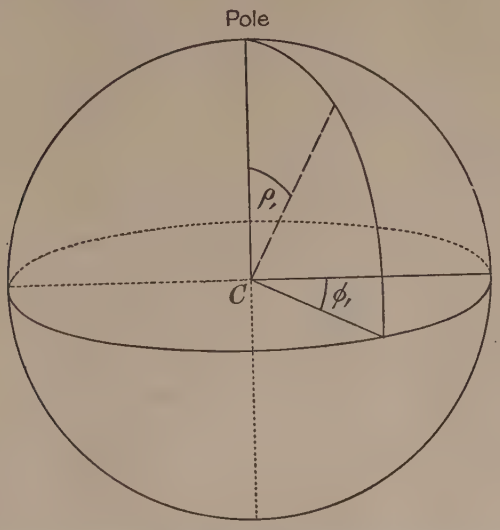


FIG. 91.—The polar coördinates ρ_1 and ϕ_1 of the normal to the plane of a face of a crystal located at C.

The actual plotting of gnomonic projections from Laue photographs (or the reverse) could be carried out in a variety of ways. It can be done

very simply and rapidly with the protractor [1] shown in Figure 92. The left side of this ruler, divided into millimeters from the central point C″, measures the distance of a Laue spot from the central image (FC′ of the preceding figures); the right side is graduated in accordance with the requirements of expression (21) to read the corresponding projected distances GC″. A different protractor is required for each distance from crystal to photograph. Data for the preparation of protractors to be used with the most common plate distances (CC′) of four and five centimeters are given in Tables I and II of Appendix II. In making a projection the appropriate ruler is mounted at C″ on a pin passing through the common center of the projection and a reproduction of the Laue photograph (Figure 93). Then since a spot and its projection lie in a line through the center C″, the projection of any spot F is located on the opposite side of the ruler at a graduation corresponding to the plate distance FC″ (FC′ of the previous figures) of the spot. The reproduction may be a tracing but it is more satisfactory to use a positive print of the Laue photograph. At the same time that a spot is projected its distance on the photograph from the central image (C″F of Figure 93) and its estimated relative intensity should be recorded. These relative intensities must be obtained from the original negative and not from prints. When five centimeters is taken as the radius of the sphere of projection, the projections of all useful Laue spots lie outside of the central area occupied by the photograph itself.

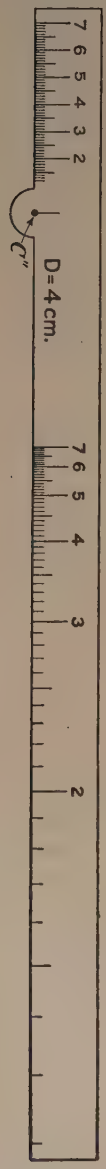


Fig. 92.—A ruler for plotting directly the gnomonic projections of Laue spots.

It has been stated that if the plane of projection is normal to an axis of the crystal, indices of faces can be read directly. Consequently the indices of reflecting planes are easily obtained on a Laue photograph made with the X-rays parallel to crystal axes. The gnomonic projection of the magnesium oxide photograph [2] of Figure 86 is shown in Figure 94. The directions of zero indices of X and of Y (the coördinate axes of the projection) are known from the crystal orientation. In a cubic crystal the axes are all at right angles to one another and of equal unit lengths so that the coördinate

[1] R. W. G. Wyckoff, op. cit.
[2] R. W. G. Wyckoff, Am. J. Sci. *1*, 138 (1921).

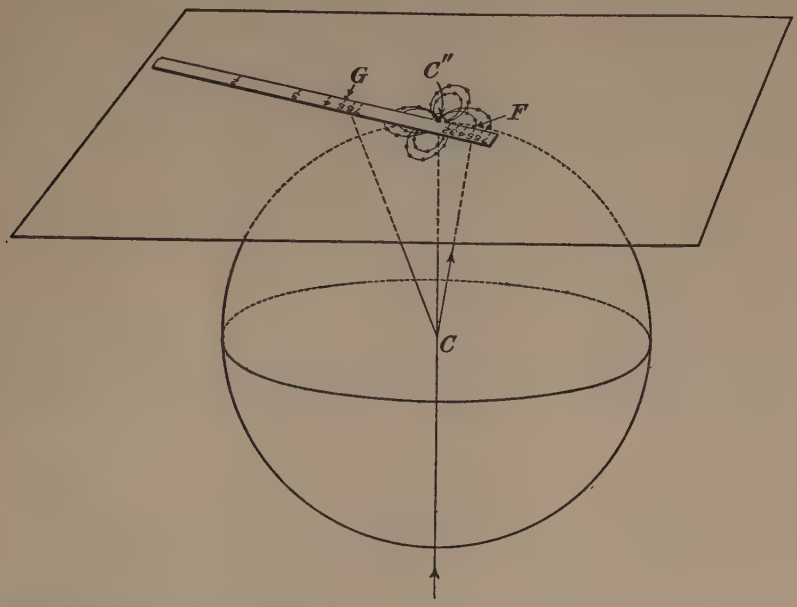


FIG. 93.—The manner of using the gnomonic ruler of Fig. 92. X-rays reflected by a crystal at C give rise to a Laue spot at F. The distance of this spot from the central image C″ is read to the right upon the ruler; its projection G lies at the corresponding division to the left of the center.

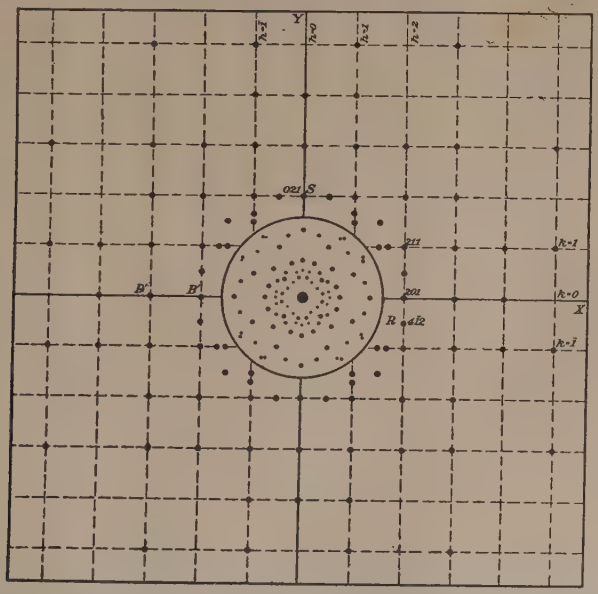


FIG. 94.—The gnomonic projection of the photograph of magnesium oxide (MgO) having the stereographic projection shown in Fig. 87. The incident X-rays are parallel to the Z-axis.

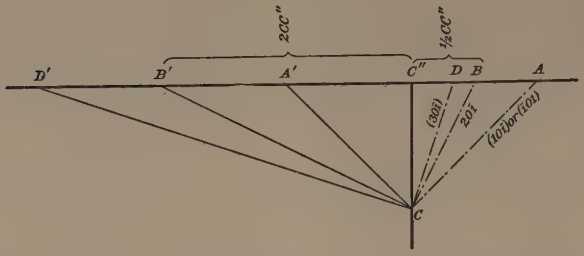


FIG. 95.—A section taken through the X and Y axes of the preceding figure. The lines CD, CB and CA are traces of the planes (30$\bar{1}$) (or $\bar{3}$01), (20$\bar{1}$) and (10$\bar{1}$). Their gnomonic projections D′, B′, A′ are so situated that D′B′, B′A′ and A′C″ are equal. For all cubic crystals they also equal CC″, the radius of the sphere of projection.

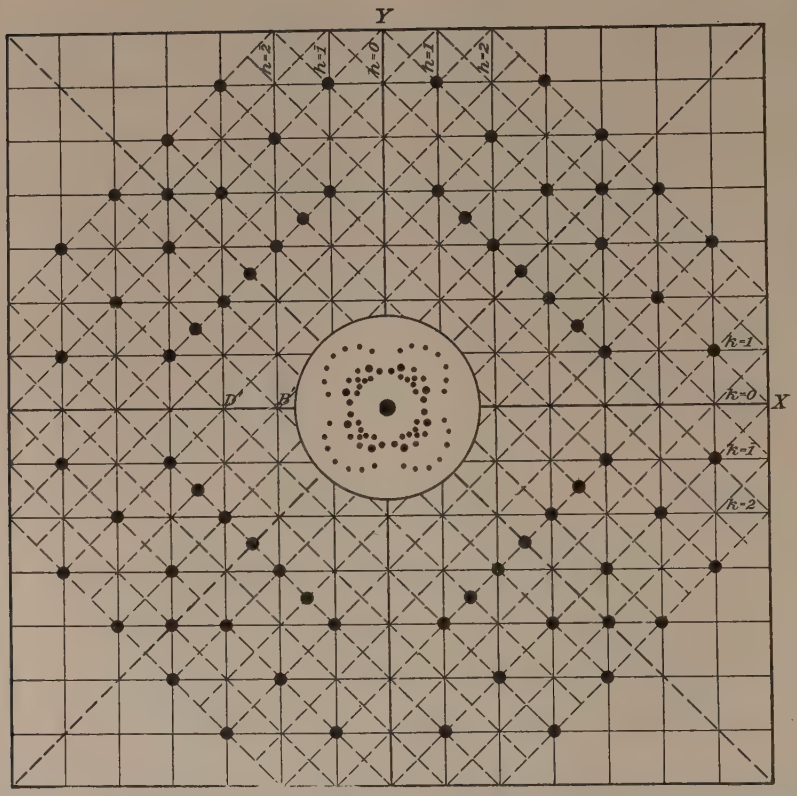


FIG. 96.—A gnomonic projection of a Laue photograph of a tetragonal crystal of rutile (TiO_2). The X-rays travel along the Z-axis. The square coördinate system of full lines corresponds to the usual axial ratio, a : c = 1 : 0.6442.

network is square. The length of the side of this network is equal to five centimeters, the radius of the sphere of projection (Figure 95). The X and Y coördinates (Figure 94) of a point give the first two indices of its corresponding plane, the Z index is always unity (as long

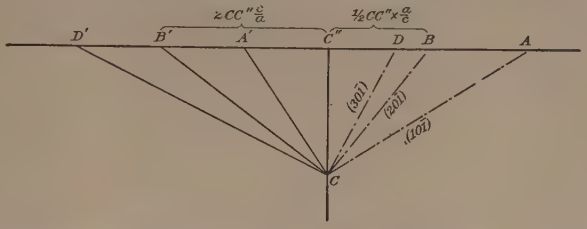


FIG. 97.—A section through the Z and X (or Y) axis of Fig. 96. The traces of certain planes of the zone (h0l)—AC, BC and DC—and also their gnomonic projections A′, B′, D′, are shown.

as the Z-axis is perpendicular to the plane of projection). If necessary the indices obtained in this manner must be multiplied by an integer to make them whole numbers. Thus the coördinates of S and of R (Figure 94) are 0X, 2Y and 2X, $-\frac{1}{2}$Y; their indices are 021 and $4\bar{1}2$ (i.e. $2\bar{1}\frac{1}{2}1$).

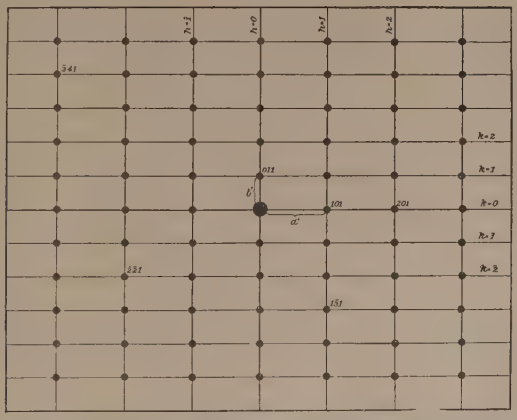


FIG. 98.—The coördinate system of a gnomonic projection of an orthorhombic crystal when the plane of the projection is normal to the principal (Z) axis.

The determination of indices on a projection (Figure 96) of a photograph taken with the X-rays traveling along the Z (c) axis of the tetragonal crystal rutile (TiO_2) is almost as simple. Since the two axes X and Y lying in a plane parallel to that of the projection are perpendicular to one another and of equal unit lengths, this coördinate net also will be square. The length of the unit side, which no longer will equal the radius

of the sphere of projection, can be obtained with the help of Figure 97. This figure shows a section normal to the projection plane which contains the Z axis (CC″) and the X (or the Y) axis of the reflecting crystal at C. The trace of the plane (10$\bar{1}$) when extended will meet the projection

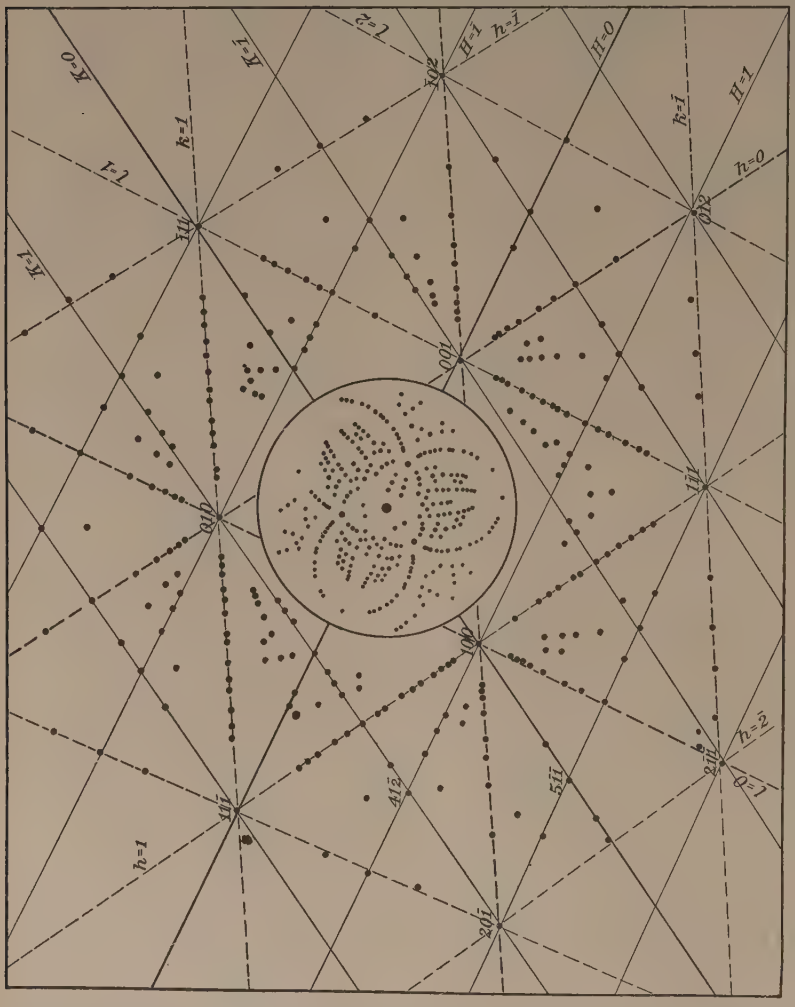


FIG. 99.—A gnomonic projection of a Laue photograph of the rhombohedral crystal rhodochrosite ($MnCO_3$) taken with the X-rays parallel to the principal (3-fold) axis. The hexagonal Miller-Bravais indices of the reflecting planes can be read with the coördinate system of full lines; their indices according to the rhombohedral Miller notation are given by the dashed lines.

plane at a point A so situated that AC″ : CC″ = a : c. The length of the side of the quadratic net is A′C″, where A′ is the gnomonic projection of A, and

$$A'C'' = CC''\frac{c}{a} = 5\ c \text{ centimeters (since a = unity).}$$

The axial ratio of rutile is a : c = 1 : 0.6442 so that A′C″ = 5 × 0.6442 = 3.22 cm.

In the projection of a Laue photograph of an orthorhombic crystal made with the X-rays parallel to the Z-axis, the coördinate system is rectangular (Figure 98). The length of its sides a′ and b′ are

$$a' = CC'' \times c/a = 5\ c/a \text{ centimeters and}$$
$$b' = CC'' \times c/b = 5\ c/b \text{ centimeters.}$$

For both hexagonal and rhombohedral crystals expressed in terms of the Miller-Bravais axes, the unit of the projection network is a rhombus having a 60° angle. This is illustrated by the full lines in Figure 99 which is the projection of a Laue photograph of rhodochrosite [1] ($MnCO_3$) prepared with the X-rays parallel to the Z axis. The length of the side, a′, of the net of this figure is governed by the relations (Figure 100).

$$BC'' = CC'' \times c/a \text{ and } a' = BC''/\cos 30° = BC'' \times \frac{2}{\sqrt{3}} \text{ or}$$

$$a' = 1.153 \times 5\ c = 5.750 \text{ centimeters (taking a = unity).}$$

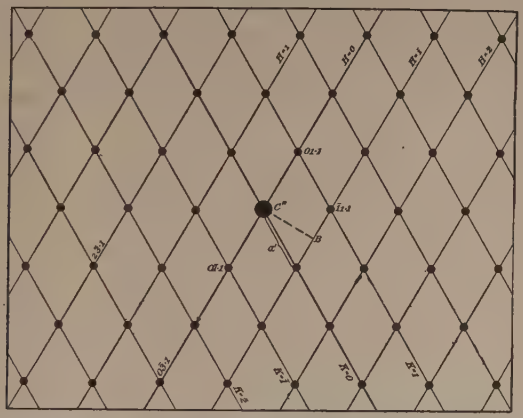


FIG. 100.—The coördinate system for the hexagonal Miller-Bravais indices of a gnomonic projection of a hexagonal or rhombohedral crystal if the plane of the projection is normal to the principal (6- or 3-fold) axis.

If the X-rays travel parallel to one of the three equivalent Miller axes of a rhombohedral crystal, the net of the resulting projection is a special case of the triclinic net. Crystals built upon the rhombohedral lattice can be first interpreted (Figure 99) in terms of the Bravais-Miller axes. These indices can then be transformed into the rhombohedral Miller indices by means of the familiar equation: [2]

$$h = 2H + K + L;\ k = K - H + L;\ l = -2K - H + L, \ldots (22)$$

[1] R. W. G. Wyckoff, Am. J. Sci. *50*, 317 (1920).
[2] See for instance P. Groth, Physikalische Krystallographie, p. 434 (1895).

where (hkl) are the Miller indices of a plane having the corresponding Bravais-Miller indices (HKIL). The Miller index field of the projection of rhodochrosite obtained in this way is shown by the dotted lines of Figure 99.

The projections of Laue photographs of monoclinic and triclinic crystals taken with the X-rays passing along crystal axes can be constructed in a similar fashion. If the projection plane is normal to the principal (Z) axis of a monoclinic crystal, the coördinate network is built of parallelograms; if it is perpendicular to the X or Y axes the net is rectangular, but the projection of the (100) or (010) plane, as the case may be, will not lie at the center of projection. The triclinic net is composed of parallelograms, the origin of which is not at the center of the projection. The only simplification of this triclinic net which results when the X-rays are parallel to a (Miller) axis of a rhombohedral crystal arises from the fact that the parallelograms become rhombs.

If the X-rays make small angles with crystallographic axes (up to 10° in some cases), parallelograms of the projection net for the resulting photographs will not be sufficiently distorted to prevent an immediate assignment of indices. This tilt may be greater if, as is a common procedure in crystal analysis, a series of photographs is prepared with gradually increased deviation from parallelism between X-rays and crystal axis.

It frequently happens that either to obtain additional data or because of the habits of growth of a crystal, Laue photographs must be prepared in which the X-ray beam makes large angles with the axes. There are various ways in which an assignment of indices can be made upon the projections of such photographs. Thus it would be possible to calculate by the usual geometrical process the positions of the projections of several important reflecting planes appearing upon the photograph. Knowing these the application of the customary zone relations would serve to locate others. The indices might also be calculated throughout in terms of their coördinate positions by a purely analytical process. If a Laue photograph is taken through some simple crystal face, it will frequently be possible to set up a new coördinate net that will aid materially in assigning indices. The photograph giving Figure 106, in which the X-rays are nearly normal to a (110) face of potassium aluminum alum, is an example. Once such a projection has been made it can also be used to shorten greatly the time required to interpret similar photographs from other crystals. The simplest generally applicable procedure consists in rotating the projection of a photograph until its plane is perpendicular to a crystal axis. In actual practice it is sufficient to rotate the projections of only a limited number of reflecting planes and thus to determine their indices. The rest

are more easily found from these by applying zone relations upon the original projection.

The plane of a gnomonic projection can be most simply rotated with the gnomonic rotation net.[1] In Figure 101 a′C is the normal to some face of a crystal located at C. If the crystal is rotated about an axis EF through C perpendicular to the plane of the great circle through B, C″ and D,

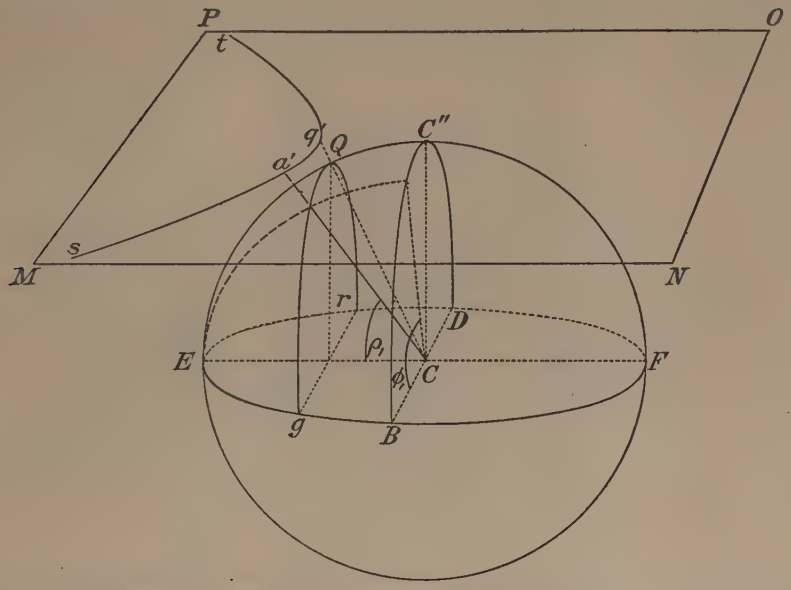


FIG. 101.—The gnomonic projection of the face of a crsytal at C is a′. If the crystal is rotated about EF as an axis, the path of the intersection of the face normal with the surface of the sphere of projection is the small circle gQr. The projected point a′ moves over the hyperbola sa′q′t. This rotation of the crystal about EF is equivalent to such a movement of the plane MNOP over the sphere that its point of tangency passes over the great circle BC″D. For the description of these rotations it is convenient to measure coördinates $\rho_1\phi_1$ (Fig. 91) from E as a pole.

the path of a′ upon the surface of the sphere of projection is the small circle gQr and its course upon the projection is an hyperbola sa′q′t. This is equivalent to such a rotation of the plane of projection MNOP that its point of tangency always lies upon the great circle through B and D. A series of great circles e′, e″, . . . (Figure 102) will measure the angle through which the crystal (or projection) has been turned and a series of small circles f′, f″, . . . will define the paths of face normals (such as sq′t of Figure 101). A gnomonic rotation net is obtained by projecting these circles upon MNOP. The great circles as usual appear as straight lines, the small circles give hyperbolas. The X and Y coördinates (ζ'

[1] H. Hilton, Mineralogical Mag. *14*, 18 (1904).

and η') of points for the construction of this net can be calculated with the following equations:[1]

$$\zeta' = CC'' \cot \phi' \qquad (23)$$
$$\eta' = CC'' \cot \rho' \operatorname{cosec} \phi'$$

where CC'', the radius of the sphere of projection, is to be taken equal to five centimeters. In these equations ρ' is measured from the point E,

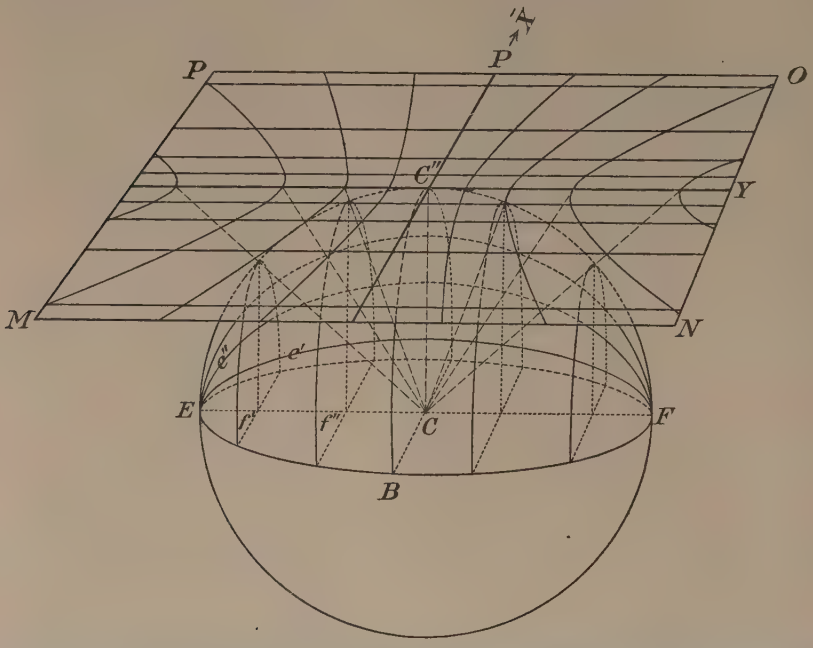


FIG. 102.—The gnomonic rotation net is obtained by projecting equally spaced small circles parallel to BC''C and an equidistant set of great circles having the axis EF.

and ϕ' from the plane of FCBE (Figure 101). The calculations[2] necessary for drawing a net which will extend to 80° can be made with expression (23). A rotation net with this wide angular range, which is essential for its use in crystal analysis, is shown[3] in Figure 103. In using it to rotate the plane of a projection, this gnomonic net (on tracing cloth or other transparent material) should be placed upon the projection so that the centers are coincident and the line joining this center with the center of the projection after rotation lies along C''P (Figures 102 and 103).

[1] G. F. H. Smith, Zeitsch. f. Kryst. *32*, 142 (1904).
[2] *Ibid.*
[3] R. W. G. Wyckoff, op. cit.

Each point upon the projection should then be moved through the angular distance between the new and old centers. Those points lying upon the line joining these two positions will obviously move along the line C″P, all other points pass over their appropriate hyperbolas.

The use of this net will be illustrated by establishing coördinate axes for the direct assignment of indices upon the (110) projection of a cubic

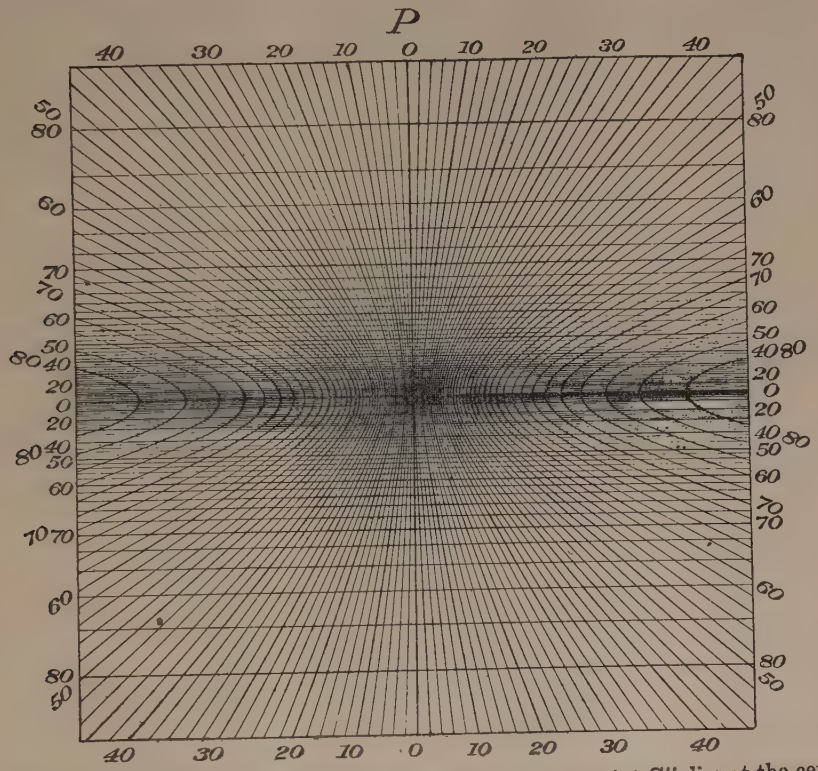


Fig. 103.—The gnomonic rotation net, extended to 80°. The point C″. lies at the center of this figure.

crystal.[1] A cubic crystal with its Z axis normal to the plane of projection gives the square coördinate network of Figure 104. When the X-rays are normal to the $(0\bar{1}1)$ face of such a crystal [$(0\bar{1}1)$ is then parallel to the plane of projection], the projection of this face will be at the center. A rotation of Figure 104 to such a position can be accomplished by placing the net (Figure 103) concentrically over this figure with the line C″P coinciding with the line h = 0 and moving each point 45° along its hyperbola. The full lines which in Figure 104 converge upon (011) will be parallel in the

[1] R. W. G. Wyckoff, Zeitsch. f. Kryst. *57*, 595 (1923).

rotated projection and furnish, as Figure 105 shows, a set of coördinate lines from which indices may be read directly. The operation of this co-

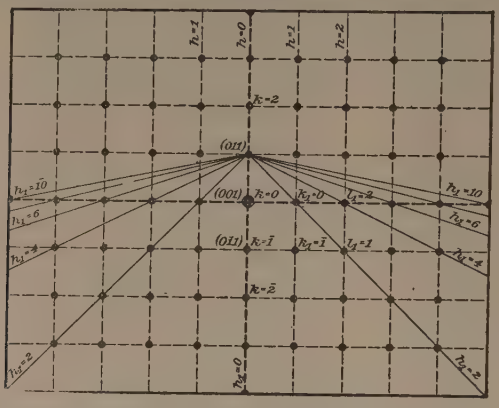


FIG. 104.—The square coordinate system (dashed lines) for the gnomonic projection of a cubic crystal when the plane of projection is normal to a four-fold axis.

ordinate system is illustrated by the projection, in Figure 106, of a Laue photograph [1] of potassium aluminum alum taken with the X-rays nearly normal to the (0$\bar{1}$1) face. Index fields for a few other special orientations have been described. Among these are to be mentioned: (a) (111)

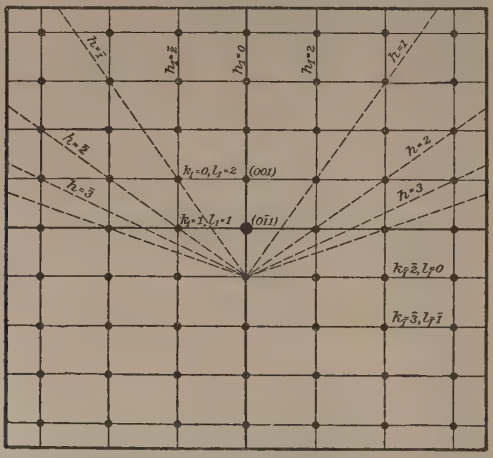


FIG. 105.—A rotation of Figure 104 till the plane of projection is perpendicular to the (011) plane. The full lines constitute a rectangular system of coördinate lines useful in assigning indices to reflecting planes in a cubic crystal oriented to give this projection.

photographs (Figure 107) of cubic crystals (analogous to basal reflections from rhombohedral crystals, Figure 99); (b) (110) photographs [2] of

[1] R. W. G. Wyckoff, Zeitsch. f. Kryst. *57*, 595 (1923)
[2] R. G. Dickinson, J. Am. Chem. Soc. *44*, 1489 (1922).

tetragonal crystals (analogous to the (110) photographs of cubic crystals); and (c) cleavage photographs of rhombohedral crystals (Figure 108).

As an illustration of the use of the zone relations (page 52) upon projections of Laue photographs, the indices of the plane P in Figure 106

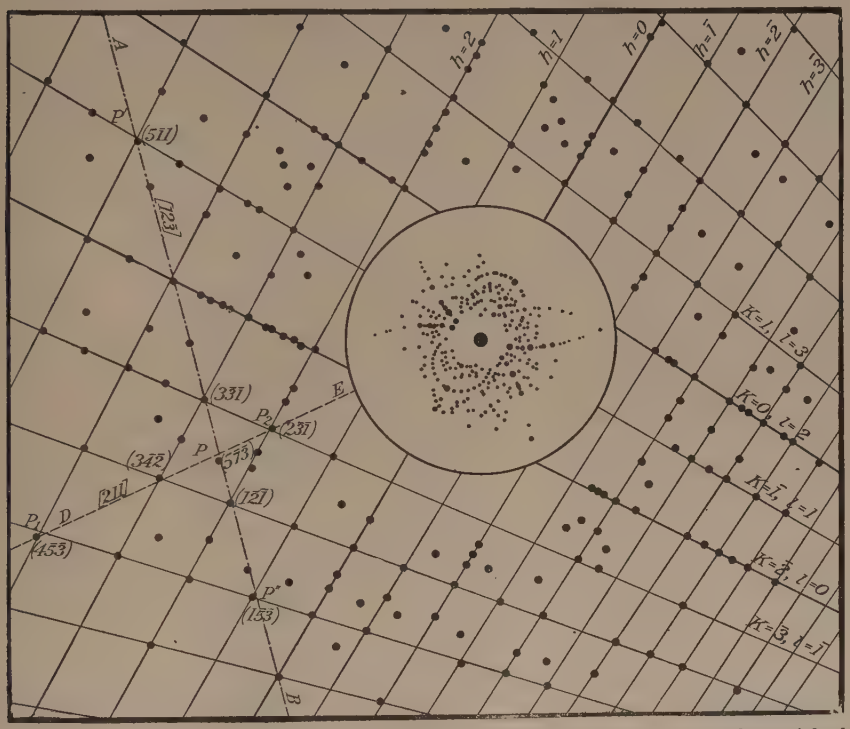


FIG. 106.—A gnomonic projection of a Laue photograph of potash alum taken with the X-rays nearly parallel to the (011) face.

may be found as follows. The indices of P′ ann P″, two points lying in the same zone AB as P, are (5$\bar{1}$1) and (1$\bar{5}\bar{3}$). Since

$$u = kl' - lk',\ v = lh' - hl' \text{ and } w = hk' - kh'$$

the zone axis symbol [uvw] for AB will be [8 16 $\bar{2}\bar{4}$] or [12$\bar{3}$]. Similarly the zone DE through P$_1$(4$\bar{5}\bar{3}$) and P$_2$(2$\bar{3}\bar{1}$) and containing P will have the symbol [$\bar{4}\bar{2}\bar{2}$] or [211]. The indices of P at the intersection of these two zones then are given by

$$h = vw' - wv',\ k = wu' - uw' \text{ and } l = uv' - vu'$$

as (5$\bar{7}\bar{3}$). Where applicable the following device is much simpler to use. It will be observed that the sum of the corresponding indices of

two planes in a zone always gives the indices of another plane lying between them in the same zone. Thus in this same Figure 106 the projection of the planes $(4\bar{5}\bar{2})$ and $(5\bar{7}\bar{3})$ will be found somewhere upon the portion of the line AB joining $(3\bar{3}\bar{1})$ and $(1\bar{2}\bar{1})$, i.e. $(2\bar{4}\bar{2})$. The indices

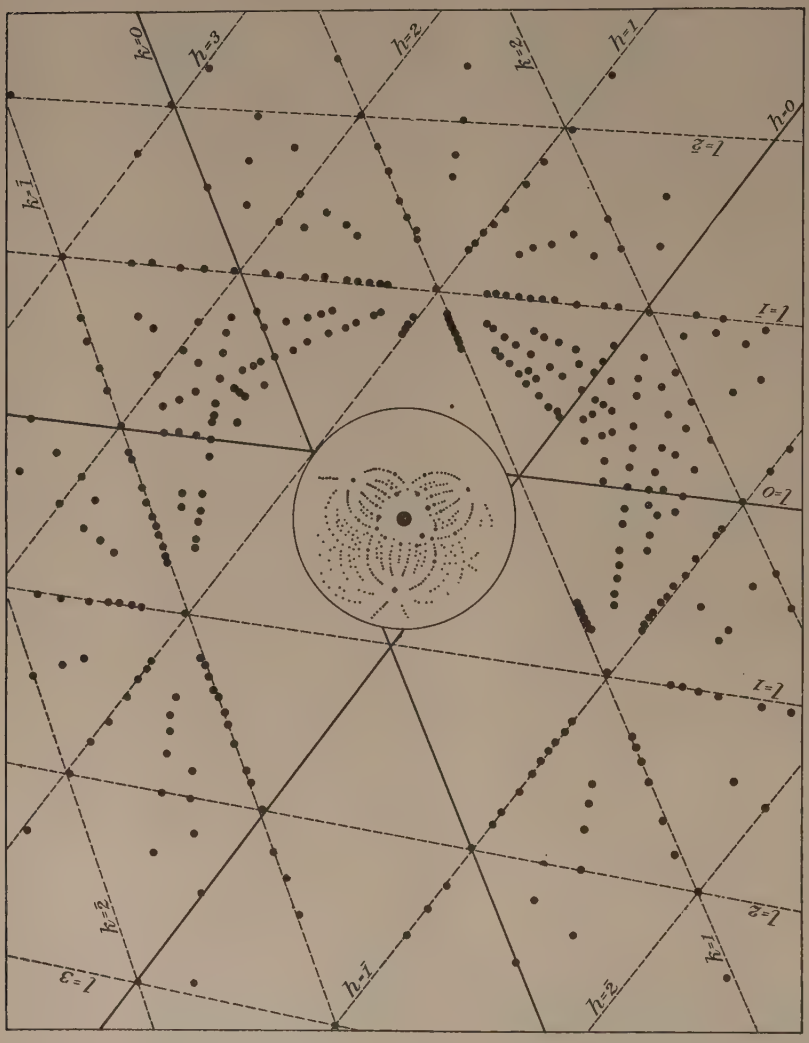


FIG. 107.—A gnomonic projection of a Laue photograph of a cubic crystal of $(NH_4)_2PtCl_6$ taken with the incident X-rays nearly parallel to a three-fold axis [or normal to a (111) face].

of P, in the zones of both AB and DE, could be found by adding together indices of points on DE until a set was obtained that was identical with one derived in a similar way from planes upon AB. Hence by adding $(2\bar{3}\bar{1})$ and $(3\bar{4}\bar{2})$ on the one hand and $(4\bar{5}\bar{2})$ and $(1\bar{2}\bar{1})$ on the other, $(5\bar{7}\bar{3})$ are

seen as the indices of P. In practice this procedure proves to be of great value and can be used whenever the indices of two planes on each of two zone lines passing through the desired point have been determined.

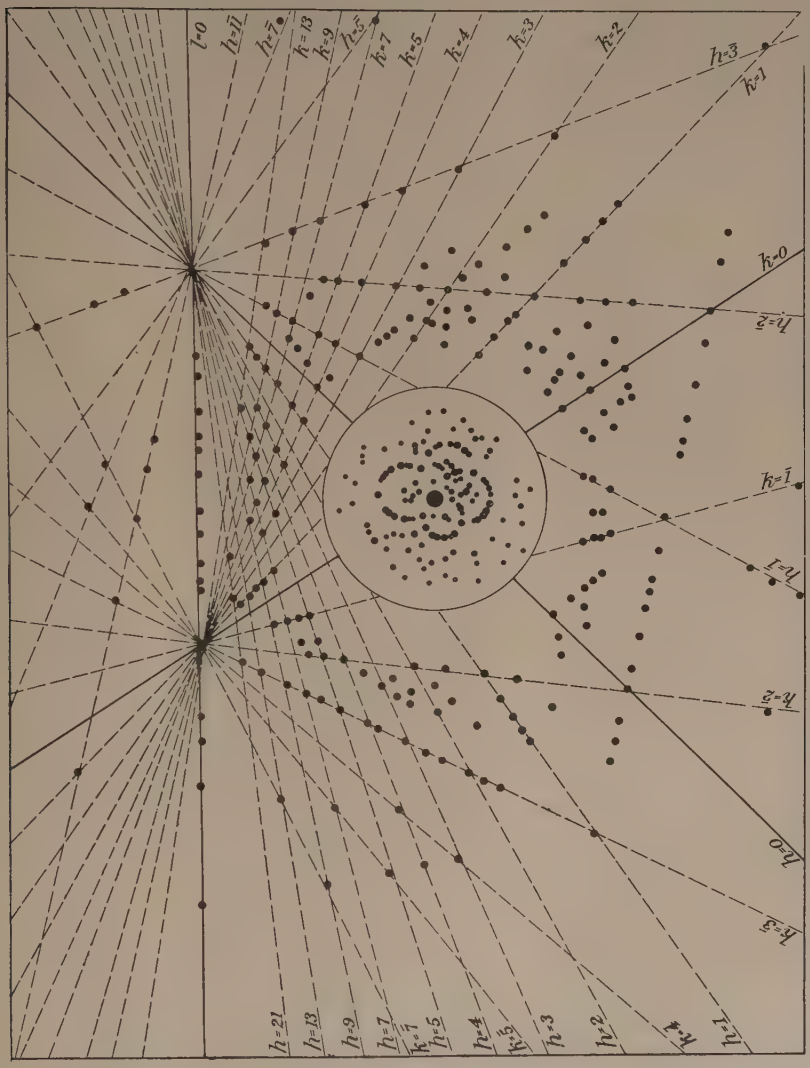


FIG. 108.—A gnomonic projection of a Laue photograph of a rhombohedral crystal of dolomite [$CaMg(CO_3)_2$] prepared with the X-rays approximately perpendicular to a (100) face.

For cubic crystals three mutually perpendicular axes of equal length can be chosen in only one way. The axes of reference are thus absolutely fixed by the symmetry requirements alone. This simple state of affairs does not prevail in any other system of symmetry. For crystals belonging

to these other systems there is an indefinitely large number of unit cells, each with different though related axial ratios, which might be chosen for crystallographic description. The indices of planes and faces will be different in terms of each of these units. This multiplicity of unit cells can be illustrated with the basal gnomonic projection [1] of tetragonal rutile (Figure 96). The unit corresponding to the full coördinate lines in this figure is the right square prism OABDO′A′B′D′ (Figure 109) where $OA = OD = a_0$ and $AA' = c_0 = 0.6442a_0$. A possible unit would, however, be furnished by the prism OBEFO′B′E′F′ in which OB is the diagonal

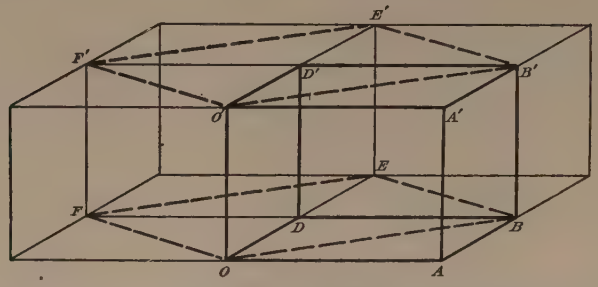


FIG. 109.—The unit cell of a crystal of rutile (TiO_2) corresponding to the axial ratio $a : c = 1 : 0.6442$ is OABDO′A′B′D′. The unit OBEFO′B′E′F′ has the axial ratio $a : c = \sqrt{2} : 0.6442 = 1 : 0.4555$. The full lines of Fig. 96 refer to the first of these, the dotted lines to the latter.

of the square OABD. The axial ratio for the new axes of this diagonal unit is $\sqrt{2}a : \sqrt{2}a : c$ and the corresponding coördinate system on the projection is given by the dashed lines of Figure 96. A transformation of indices from one coördinate set to another thus is readily carried out upon the projection. The relation between the indices of a plane referred to two axial systems can also be expressed by simple equations of a form deducible from the projection. For instance if (hkl) are the indices of a plane according to the original axes of Figure 96, the indices (h′k′l′) of the same plane referred to the diagonal set are given by

$$h' = h + k,\ k' = k - h,\ l' = l.$$

Still other unit cells would be obtained by multiplying either the a or the c axis of the original unit or its diagonal derivative by an integer.

In the hexagonal system an indefinite number of units diagonal to one another are possible, as well as the ones obtained by multiplying one or the other of the axial lengths of these units by an integer. In the orthorhombic system there is only one way of setting up three mutually perpendicular axes of reference; their relative lengths as sides of possible unit

[1] From unpublished data by the writer.

cells may, however, be pa : qb : rc, where a : b : c is an axial ratio and p, q and r are any integers. Conditions are still more complicated for monoclinic and triclinic crystals because then unit cells can be developed from sets of axes which not only make different angles with one another but can vary in the unit lengths of all three axes. The problem of determining which of this large number of conceivable units are compatible with the prevailing atomic arrangement presents one of the greatest difficulties encountered in studying the structures of crystals of low symmetry.

The Determination of the Wave Lengths of X-rays Producing Laue Spots.[1]— After indices have been assigned, the wave length of the X-rays producing each spot in a Laue photograph can be determined with the appropriate form of expression (16) of Chapter III:

$$n\lambda = \frac{2a_0}{\sqrt{F(hkl;\ abc;\ \alpha\beta\gamma)}} \sin \theta_n$$

Sin θ_n can be calculated by remembering that the distance of a spot from the central image divided by the distance from crystal to photograph equals the tangent of $2\theta_n$. In the routine analysis of Laue photographs it is an advantage to be able to step directly from plate distance to sin θ using a conversion table (see Table III, Appendix II). Distances of the individual Laue spots, as read upon the right hand side of the gnomonic ruler, are recorded during projection in order to be available for this calculation of sin θ. A rough estimation of the length of the edge of the unit cell can be obtained from Laue photographic data alone but it is much more satisfactory to get it accurately from a spectrometric observation of some sort. If the crystal is cubic, the correct values of $n\lambda$ for each spot can be immediately calculated from the data. The uncertainty concerning the choice of a suitable unit in crystals of lower symmetry introduces difficulties which will be mentioned subsequently.

At voltages suitable for making Laue photographs the intensity of X-rays increases with wave length from the zero defined by the quantum condition to a maximum and then gradually falls off again (Figure 58). The position of this maximum shifts towards shorter wave lengths as the voltage upon the X-ray tube is raised. The photographic effect of X-rays of various wave lengths (page 85) on the other hand parallels their absorption in the silver bromide emulsion, rising to a maximum at the absorption limit for silver, and then after a sharp fall, mounting to the bromine limit. The curve outlining the photographic effect of the "white" X-rays producing Laue patterns arises from a compounding of these two curves.

[1] The basis of this method of interpreting Laue photographs for the study of crystal structures was laid by P. P. Ewald, Ann. d. Physik *44*, 257 (1914).

Its general character [1] for X-rays from a tungsten tube operated at 40,000, 50,000 and 60,000 volts is given by Figure 110. Each curve rises rapidly from the short wave length limit and reaches a maximum around a wave length of 0.484 A° (the characteristic absorption limit of the silver). This peak is more marked and the long wave length portion less important at 60 than at 40 kilovolts. The broadening of this maximum due to

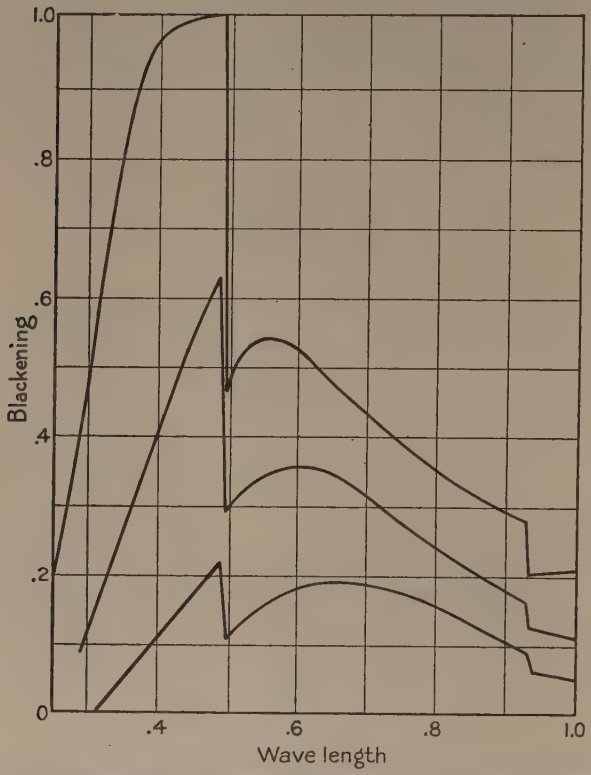


FIG. 110.—Curves showing the photographic effect of the "white" radiation from a tungsten tube. The top curve has been calculated for an applied voltage of 60 K. V., the middle one for 50 and the bottom one for 40 K. V.

the continued shift of the X-ray intensity curve (Figure 58) toward the short wave length region is becoming important at 60 kilovolts. At still greater potentials the maximum photographic effect will no longer remain at the critical absorption of silver but will shift towards shorter wave lengths.

In general, reflections to be used in establishing the structure of a crystal should involve wave lengths between the low wave length limit,

[1] R. W. G. Wyckoff, Am. J. Sci. *50*, 317 (1920).

λ_{min}, and $2\lambda_{min}$. Otherwise if $n\lambda > 2\lambda_{min}$ an observed reflection may be partly of one and partly of another order. Only when it is known in some other way that planes of particular types do not give reflections in the first one or more orders can higher values of $n\lambda$ be safely employed in intensity comparisons. If a high tension transformer supplies the current, Laue photographs are most efficiently produced at 50 to 60 kilovolts; at this potential the maximum of the wave length — intensity curve is practically coincident with the critical absorption of silver but there is no appreciable radiation shorter than $\lambda_{min} = \frac{1}{2} \times 0.48$ A°. In higher voltage photographs the existence of wave lengths less than 0.24 A° will render valueless the potentially intense reflections near to $n\lambda = 0.48$ A°. With strongly absorbing crystals, however, it may be necessary to forego the use of these strong reflections and work at a higher potential for the sake of the more penetrating radiation.

A knowledge of the low wave length limit in the X-ray beam can be used to eliminate many of the crystallographically possible unit cells of a non-cubic crystal. Values of $n\lambda$ for each of these units can be calculated in the manner already outlined. All those units may be discarded which do not give values of $n\lambda$ down to but not below λ_{min} [unless the presence of a critical absorption limit (see below) in the region from λ_{min} to $2\lambda_{min}$ causes the absorption of these shortest wave lengths]. The application of this criterion will be illustrated in Chapter VII.

A photograph taken with the X-rays inclined at an angle of a few degrees to a crystal axis yields the greatest amount of valuable information. In such a photograph planes belonging to the same form will occur at different distances from the central undeviated spot and consequently will be reflecting X-rays of different wave lengths. If the diffracting crystal is composed of atoms which do not have a critical absorption limit between λ_{min} and $2\lambda_{min}$, a smooth curve will be obtained by plotting against their wave lengths the estimated intensities of the reflections from all planes belonging to one form. This curve is similar to the ones showing the photographic effect of "white" X-rays (Figure 110). Several such curves [1] for forms giving reflections in a photograph of magnetite (Fe_3O_4) are illustrated in Figure 111. Enough reflections for the construction of these curves will be found on a single photograph only for crystals with high symmetry. Their shape must be borne definitely in mind, however, whenever intensity comparisons are attempted between reflections due to different wave lengths. As Laue photographs are usually prepared, the planes reflecting the same wave lengths and the useful data obtained from any one photograph will be in a sense an affair of chance. This uncertainty is not necessary for it is clearly possible to

[1] S. Nishikawa, Proc. Math. Phys. Soc. Tokyo *8*, 199 (1915).

calculate in advance the particular position of a crystal required to make two reflections have the same wave length. Such an accurate placing of the crystal is, however, rarely required at the present time.

Serious attempts have not been made to measure accurately the intensities of Laue spots. This is partly due to the fact that the large range of blacknesses to be measured and the varying size of the individual spots make the photometering a difficult problem. Furthermore quantitative intensity data, even if they were available, could not now be interpreted directly in terms of atomic positions. It has been the custom

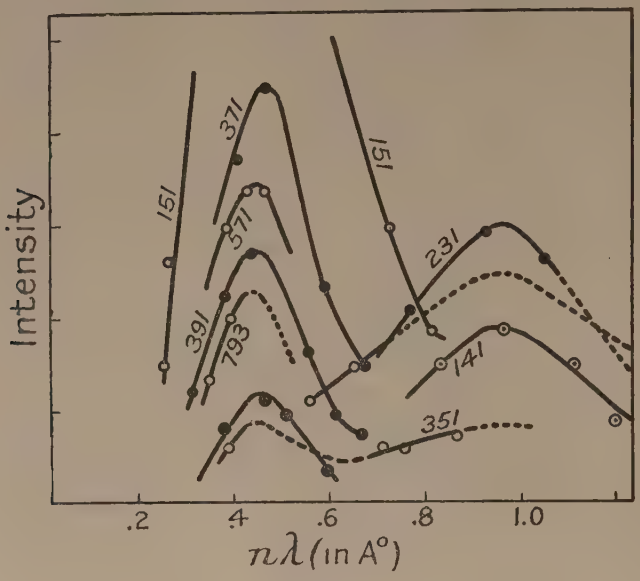


FIG. 111.

simply to assign relative intensities by visual estimations upon the photographic negative. For many purposes it is merely necessary to divide spots into three groups — those that are strong, of medium intensity, or faint. The possibility of expressing more grades of intensity difference is presented by using a number scale, which usually takes ten as its upper limit. The divisions of this scale frequently have had no physical significance; they can in cases where this refinement seems justified be based upon a standard consisting of a series of timed direct exposures to X-rays. The only intensity estimations more accurate than these assignments which are now required in crystal structure determination are relative comparisons of pairs of reflections; such determinations of relative strength can be made visually with great certainty. The accurate photometry of Laue spots, in common with the quantitative development of so many

other topics in crystal analysis, waits for an increase in knowledge of the laws of scattering.

Absorption will have a marked influence upon the intensity of Laue spots. Rays diffracted through large angles travel farther in the crystal (if the X-rays are normal to the faces of the crystal section) and consequently are subject to a greater loss in intensity. The effect of absorption must always be taken into consideration when making relative comparisons of intensity unless the two spots under consideration are reflected through the same angle θ. If a crystal contains one or more atoms having critical absorption limits in the useful range between λ_{min} and $2\lambda_{min}$, the intensity of reflection of a plane for different wave lengths will no longer follow such simple curves as those of Figure 111. As a result of the strong absorption immediately below the critical absorption limit, curves plotted from Laue photographs will have a shape more like that of the curve of Figure 112. Reflections of shorter wave lengths register themselves only faintly, if at all. Great care must be exercised in any intensity

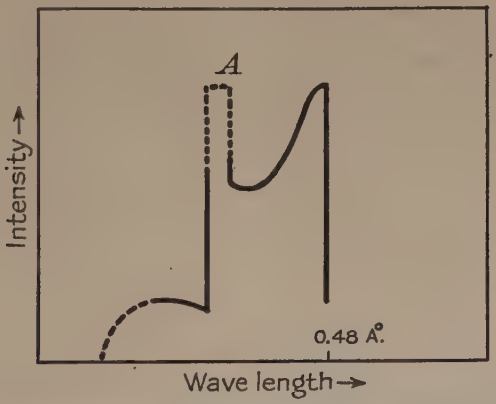


FIG. 112.—A curve illustrating the probable way in which the intensity of reflection from planes of a single form varies with the wave length if the crystal has a critical absorption in the useful region.

comparisons made within this region of selective absorption. If, as recent experiments [1] appear to prove, there is in some instances a strong reflection of X-rays with wave lengths equal to those of the characteristic lines of the scattering crystal, the ordinate of A of Figure 112 may be sufficiently heightened so that it, rather than the characteristic silver absorption, may give the maximum effect in a Laue photograph.

The Monochromatic Laue Photograph.[2] — The large number of different

[1] G. L. Clark and W. Duane, Proc. Nat. Acad. Sci. *9*, 126 (1923).

[2] Photographs of this type have been made by the writer over a period of several years but an account of their properties has never been published.

wave lengths producing reflections materially limits the useful data to be obtained from a single Laue photograph. If one were prepared in the usual manner but with monochromatic X-rays, few crystal planes would be in the proper position to reflect and the resulting pattern would consist of a very limited number of spots. If, however, the crystal specimen were kept in continual rotation one plane after another would be brought to reflect this monochromatic beam. As a consequence a Laue photograph rich in spots would be obtained in which each reflection was due to waves of the same length. A beam of practically monochromatic X-rays can be produced [1] with a molybdenum target tube by absorbing all X-rays but the most intense doublet in the characteristic K-series of molybdenum with a zirconium filter. The indices of the planes producing the spots observed in one of these photographs can be found by using the gnomonic rotation net to follow the paths of the crystal planes during rotation. It is, however, a much more lengthy procedure than the index determination in a simple Laue photograph.

In spite of the desirability of having all of the reflections of the same wave length, this mode of experimentation possesses disadvantages which have not encouraged its general use as yet. A good photograph can only be prepared from crystals which are very perfect internally. The long wave lengths of the K-lines of molybdenum, as the only monochromatic radiation available, are strongly absorbed in passing through the crystal and even more care than usual is required in making intensity comparisons between reflections that have passed through different thicknesses of crystal. Furthermore the continuous rotation of the crystal leaves any one plane in a position to reflect for such a short period that very long exposures are required to register the fainter spots. Monochromatic Laue photography, nevertheless, may be valuable after an increase in knowledge of scattering has put a more definite value upon single observations.

Anomalous Diffraction in Laue Photographs. — Diffraction effects which are not to be accounted for as reflections from atomic planes in a perfectly constructed crystal are encountered upon many Laue photographs.[2] In photographs from strained crystals the usual Laue spots are drawn out into radial streaks. Similar, but less strongly marked, streaks passing through principal zones of spots are also observed from such comparatively poor crystals as the alkali halides. It has been suggested [3] that these stripes are essentially powder photographs produced by minute crystals in positions which deviate somewhat from parallelism with the

[1] A. W. Hull, Phys. Rev. *10*, 661 (1917).

[2] F. Rinne, Ber. Sächs. Akad. Wiss. Leipzig (Math-phys. Klasse) *67*, 303 (1915); G. Aminoff, Geol. För. Förh. *41*, 534 (1919); E. Hupka, Physikal. Z. *14*, 623 (1913); F. M. Jaeger, Proc. Roy. Acad. Amsterdam *18*, 3; etc.

[3] For instance, R. G. Dickinson, Phys. Rev. *22*, 199 (1923).

main body of the crystal. In two instances — potassium iodide [1] and tin tetraiodide [2] — the intensities of these streaks are largely localized in ill-defined spots. The appearance of these "hazy" diffractions is very different from that of true "reflections" and with crystals that are good enough for satisfactory crystal structure investigation there is no possibility of confusing the two phenomena. Besides these diffraction effects, undoubtedly due to distortions or irregularities in the crystalline arrangement, "anomalous" results have been found from spectrometric observations [3] on potassium iodide crystals. Similar anomalies are described [4] in photographs resembling Laue photographs. These photographs, which were prepared with an X-ray beam defined by passage through only one pin-hole slit, showed spots which are considered not to be reflections from any crystal planes. None of these photographs have yet been analyzed in the usual manner to identify the reflections which actually occur and the published specimen photographs are too poor to permit of such an analysis being made upon them. These "anomalous" effects are not the same as those observed upon true Laue photographs of either potassium iodide [5] or tin tetraiodide.[6] As yet they have never been obtained under the experimental conditions ordinarily used in making Laue photographs for crystal structure investigations. Not only the failure to find them from other kinds of crystals,[7] but particularly the known imperfections of crystalline potassium iodide suggest that, like the well-known hazy diffractions from these crystals, they may not be properties of perfectly constructed crystals. Furthermore the fact [8] that the "anomalous" spots are proportionately much more weakened than are regular reflections when a second defining slit is introduced indicates that they are not to be expected upon true Laue photographs (which are made with *parallel* beams of X-rays).

Summary. — A generally useful method has now been outlined for interpreting the reflection spots in Laue photographs. If the length of the side of the unit cell has been determined by some other procedure, then the wave lengths of the several hundred reflections found upon an ordinary Laue photograph can be calculated. Among these there will be a considerable number which are produced by X-rays for which $n\lambda$ lies between λ_{min} and $2\lambda_{min}$ and which consequently provide a large mass

[1] R. W. G. Wyckoff, Science *58*, 52 (1923); Am. J. Sci. *6*, 277 (1923).
[2] R. G. Dickinson, J. Am. Chem. Soc. *45*, 958 (1923).
[3] G. L. Clark and W. Duane, Proc. Nat. Acad. Sci. *8*, 90 (1922); etc.
[4] G. L. Clark and W. Duane, J. Opt. Soc. Am. *7*, 455 (1923) and recently Proc. Nat. Acad. Sci. *10*, 48 (1924); Science *58*, 400 (1923).
[5] R. W. G. Wyckoff, Science *58*, 52 (1923); Am. J. Sci *6*, 277 (1923).
[6] R. G. Dickinson, J. Amer. Chem. Soc. *45*, 958 (1923).
[7] R. W. G. Wyckoff, Science *58*, 52 (1923); Am. J. Sci. *6*. 277 (1923).
[8] G. L. Clark and W. Duane, J. Opt. Soc. Am. *7*, 455 (1923) and recently Proc. Nat. Acad. Sci. *10*, 48 (1924); Science *58*, 400 (1923).

of data available for use in crystal analysis. An outstanding advantage of the Laue photographs for this purpose arises from the fact that it is possible with these many reflections from planes with complicated indices to make intensity comparisons between planes of different forms to which the same kinds of atoms contribute but which still have the same or closely similar spacings. Thus the uncertainties concerning the laws governing the scattering of X-rays (Chapter III) are eliminated as far as possible.

If the length of side of the unit cell is not found by another procedure it could still be approximately determined from a use of the short wave length limit, λ_{min}, as calculated from the impressed voltage. In practice this is unnecessary because whenever a Laue photograph can be prepared a spectrometer measurement is possible. The knowledge of λ_{min} is useful, however, in deciding between the different unit cells possible for other than cubic crystals.

Chapter V. X-Ray Spectrometry and Spectroscopy

X-ray Spectrometry

In accordance with equation (16) of Chapter III,

$$n\lambda = 2d_{hkl} \sin \theta_n,$$

a beam of X-rays AB (Figure 113) incident upon a crystal face CC_1 will be reflected at certain angles, and at these angles only. An X-ray spectrometer is an instrument which determines the ratio $n\lambda/d_{hkl}$ by measuring the angle θ_n of reflection of the X-rays from individual crystal faces. If the wave lengths of the rays are known, this ratio will give the absolute distances between physically (but not necessarily geometrically) alike atomic planes in different crystals; or, if the same crystal face is employed, this ratio will measure the relative lengths of X-rays from different sources.

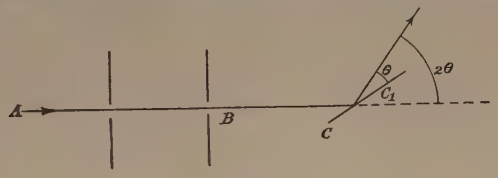


FIG. 113.

Studies of atomic arrangement are concerned with only the first of these two uses.

Any X-ray tube which is emitting the characteristic radiation of its target could be used directly in spectrometric observations upon different crystals. Hot-cathode tubes with tungsten and molybdenum anticathodes are the only ones commercially available. Of these molybdenum is the more satisfactory. The L-radiation of tungsten is very complicated; it is also of so long a wave length that it reflects through too large angles and is too readily absorbed. Tungsten K-radiation, on the other hand, is excited at too high a voltage to be conveniently used in most experimental arrangements. Other X-rays than the K-series lines of molybdenum have been used in the past. Notable amongst these are the K-lines of rhodium, iridium, palladium and platinum.

Apparatus. — The usual form of X-ray spectrometer [1] consists essentially of a set of one or more slits to yield a confined beam, a table upon which the crystal can be mounted at a desired angle, and lastly an ioniza-

[1] W. H. Bragg and W. L. Bragg, Proc. Roy. Soc. A. *88*, 428 (1913); X-rays and Crystal Structure, Chapter III (London, 1918).

tion chamber for the detection and measurement of the rays reflected from the crystal face. Figure 114 illustrates the arrangement of these essential parts in an instrument capable of furnishing approximate measurements. The distance of the second (S_2) of the two slits (S_1 and S_2) of variable widths

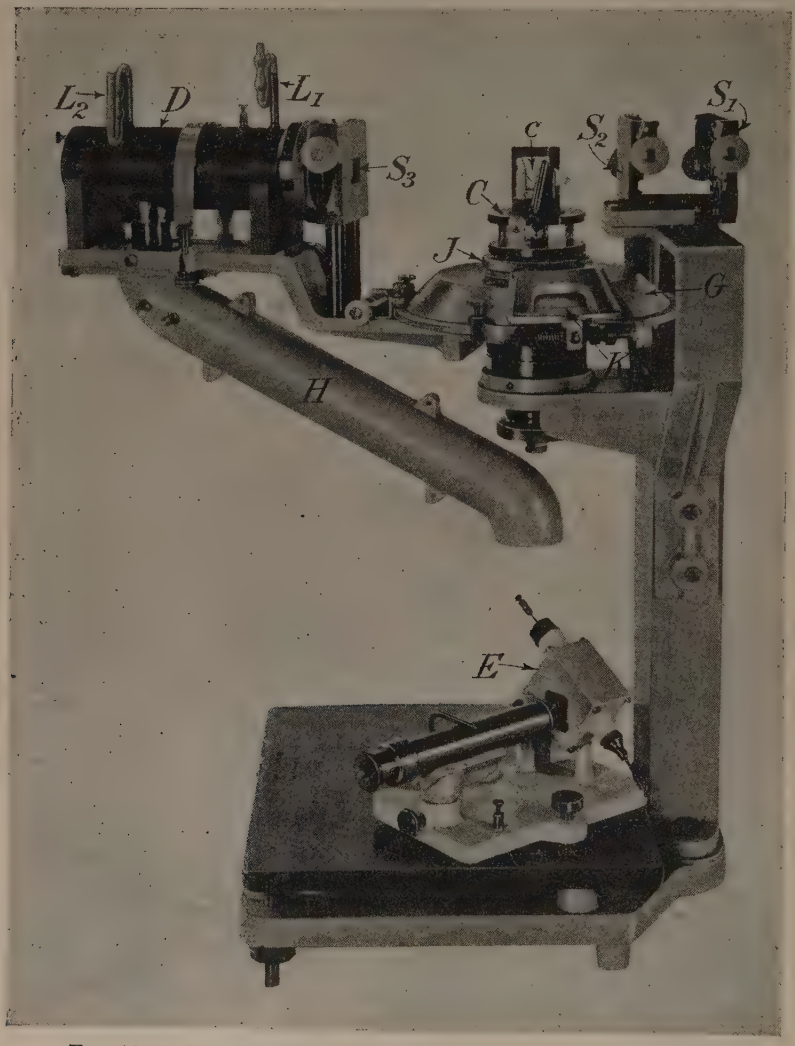


FIG. 114.—A photograph of a rough form of the X-ray spectrometer.

from the crystal table C can be altered at will. The crystal specimen to be examined is mounted with wax upon a holder standing on the spectrometer table. This holder can be tilted to bring the plane of the slit beam

of X-rays and of the correct crystal face into coincidence. If a large crystal is available the face from which the reflection is to be taken can be mounted in place with the aid of a removable templet. With a crystal too small to cover the entire X-ray beam it is often desirable to limit the exposed crystal surface with an opening of definite size. A variable diaphragm made for this purpose from platinum foil is shown at c. For many measurements it is more accurate to study the internal reflections obtained by passing the X-rays through a thin section of crystal rather than reflecting them from a developed face. The crystal holder should also be fitted with a pin or other device for locking it in a definite and reproducible position upon the table arm J; in this way the angular position of the crystal can be exactly defined by the vernier K reading upon the graduated circle G. Reflected X-rays pass through the defining slit S_3 of variable width into the ionization chamber (D) by a window covered with aluminum foil or mica. In this spectrometer of Figure 114 the ionization chamber is a brass cylinder about 5.5 cm. in diameter and 16 cm. long. The internal electrode is a brass rod running longitudinally along the tube immediately out of the direct path of the entering rays and insulated from the case by a plug of sulfur. This electrode is connected with an electroscope (E) by a wire passing through the earthed shield H. A voltage of about 400 volts (furnished by a battery of primary cells or storage cells of small capacity) is impressed upon the case of the ionization chamber. The chamber itself is filled with some gas (such as sulfur dioxide or methyl bromide) which absorbs the X-rays strongly. The current which results from the ionization of this gas by entering X-rays flows between the charged case and the previously earthed electrode-electroscope system. The consequent change in the potential of the latter, as read by the electroscope, measures the intensity of X-ray reflection. In making such an observation of intensity it is customary to break the earthing key, after turning on the X-rays,[1] and to observe the deflection of the leaf with a microscope and scale. In Figure 114 the electroscope is of the "tilted" type. In general, however, better results will be obtained by using a quadrant electrometer instead of an electroscope. In bringing the parts of the spectrometer into alignment it is often convenient to have both the front window of the ionization chamber and also a small rear window covered with mica or very thin glass.

The ionization chamber should be prepared for use by passing the ionizing gas through it until most of the air has been displaced. At L_1 and L_2 are shown mercury traps that are useful for controlling the flow of

[1] Before spectrometric observations can be made it is necessary that the tube be warmed up until the source of X-rays no longer changes its position by expansion of the target. For this reason it is better to keep the tube running continuously and to use a lead shutter to control the time during which the X-rays strike the crystal.

this gas and reducing its subsequent loss. Methyl bromide liquefies at + 4.5°C and may be safely kept liquid in sealed tubes at ordinary temperatures. Its passage into an ionization chamber is readily controlled with the aid of an ice bath. If it should be desired to make observations upon relative intensities of reflections which involve more than a single wave length, it must be remembered that the absorbing power for any gas, and consequently the ionization, is different for different wave lengths. In such cases electroscope or electrometer readings can not be taken directly as measures of intensities of reflection unless the ionization chambers are made of sufficient length to absorb all of the incident X-rays. This variation of ionization with wave length will be particularly marked with methyl bromide for rays in the neighborhood of the K-radiation of molybdenum because of the nearness of the latter to the characteristic absorption limit of bromine.

It is a point of importance not only to X-ray spectrometry but also to X-ray spectrography that if the distance from the crystal to the slit source is equal to the distance from the crystal to the indicating device, there will be a focusing of reflected X-rays of a definite wave length at the latter, even when the original beam is quite divergent.[1] In Figure 115, O is the slit source and A is the ionization chamber slit (S_3 of Figure 114). The axis of rotation (B) of the crystal face is so placed that

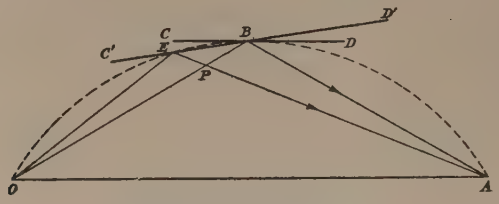


Fig. 115.

OB = BA. In the position CD of the face, the angle CBO is equal to the angle DBA and the ray reflected by CD passes along the line BA. It can be shown[2] that with the face turned about B into another position C′D′, the angles C′EO = D′EA = CBO; consequently X-rays of the wave length that passed along BA will travel along EA for the new crystal position and will be focused at A.

[1] W. H. and W. L. Bragg, X-rays and Crystal Structure, p. 31.

[2] The $\triangle EOP$ and BPA are similar because $\angle EPO = \angle BPA$ and $\angle OEA = \angle OBA$. $\therefore \frac{OP}{PA} = \frac{EP}{PB}$. $\therefore \triangle EPB$ and OPA are similar and $\angle BEP = \angle BOA$. $\angle BEP + \angle AEO + \angle OEC' = 180° = \angle ABO + \angle BAO + \angle BOA = \angle AEO + \angle BAO + \angle BEP$ (from above). $\therefore \angle OEC' = \angle BAO$. If $OB = BA$, then $\angle BOA = \angle BAO$ and $\measuredangle DBA = BEA = CBO = C'EO$. Thus the rays reflected by CD and $C'D'$ at B and E both pass through A

Problems of Accurate Spectrometry for Crystal Analysis. — Two measurements are made with the spectrometer upon a reflection from a crystal face — a record (1) of its intensity and (2) of its position.

It is not easy to obtain reliable estimates of intensity under the usual experimental conditions. One reason for this lies in the irregularities in the current that can be put through the X-ray tube unless elaborate and costly sources of high potential are available. To avoid these changes each observation could be made a comparison measurement against the simultaneous reflection from some standard crystal face. Such a procedure requires essentially two spectrometers, one of the general type that has been described, the other a simpler one which permits of a permanent setting upon some important reflection from the standard crystal face, such as the cleavage face of calcite. The ionization chambers of these two spectrometers must not change their properties if reproducible results are to be obtained. Such practically constant and permanent chambers can be made of glass or fused silica. It has recently become possible to obtain stabilizing devices designed to hold the current through the X-ray tube constant. Their use makes a comparison spectrometer unnecessary for many purposes. Best results are, however, only to be expected through the use of a source of constant high potential.

Another serious difficulty in the way of accurate intensity measurements from a crystal face arises from the fact that the amount of the reflection is strongly influenced by the physical state of the face. Not only the total reflection but the relative intensities in different orders will be markedly different from a cleavage surface than from one which has been polished. This is clearly shown [1] by the following data (Table I) upon second-order reflections from the (100), cleavage, face of rock salt.

TABLE Ia

Crystal	Intensity
1. From an excellent cleavage face	50.8 units
2. From another cleavage face—	
a. When the cleaved edge is horizontal	25.4
b. When the cleaved edge is vertical	12.9
3. From the crystal of 2 after polishing	100

TABLE Ib

Crystal	Intensity		
	Second order	Fourth order	Sixth order
2. (above) after polishing	100 units	18.4	4.1
1. (above) not polished	50.8	18.1	4.7

[1] W. L. Bragg, R. W. James and C. H. Bosanquet, Phil. Mag. *41*, 309 (1921).

A similar increase in intensity on polishing has been observed not only with cleavage surfaces of calcite but also from natural (not cleavage) faces of crystals of sodium chlorate and sodium bromate [1] grown from solution.

Some experiments [2] have been made with a double spectrometer which bear upon the influence of perfection of crystal face upon the intensity of X-ray reflection. In such a spectrometer the X-rays suffer successive reflection from two crystal faces. If the two crystals are alike, a maximum reflection will be obtained when their faces are strictly parallel; if the crystals providing these reflecting surfaces are not perfectly constructed, reflection of a single wave length does not occur sharply at one angular position and appreciable effects will be recorded as the second crystal moves about its position of parallelism with the first. The height and breadth of the "rocking curves" resulting from such rotations are measures of the intensity of reflection from a crystal and of the perfection of its reflecting face. By this experimental method it has been shown that calcite is a much more perfect crystal than rock salt. The apparently greater reflectivity of the latter is due not to a greater reflecting power but to its more imperfect character. A similar explanation probably holds for the apparent increase in reflecting power after grinding and polishing crystal faces — thus, the rocking curves [3] of calcite and rock salt cleavage surfaces become less high but much broader after polishing.

It has also been found [4] that unless an artificially prepared face is so ground that it is absolutely parallel to the corresponding atomic planes there will be a different intensity of reflection depending upon whether the crystal is mounted to turn clockwise or counterclockwise for reflection. The magnitude of this difference is shown by the data [5] of Table II which

Table II

Orientation	Intensity		
	Second order	Fourth order	Sixth order
Right hand rotation	100 units	61.0	41.5
Left hand rotation	52	38.9	39.5

were obtained from a crystal face of ruby (Al_2O_3) that was inclined 1°49′ to the ($1\bar{1}0$) planes. Similar measurements upon a face of rock salt which was within half a degree of being parallel to the (100) planes are shown in Table III. When the reflecting surface is not parallel to the atomic planes in the crystal, the angle of incidence of the X-rays with

[1] R. G. Dickinson and E. A. Goodhue, J. Am. Chem. Soc. *43*, 2045 (1921).
[2] B. Davis and W. M. Stempel, Phys. Rev. *17*, 608 (1921); *19*, 504 (1922).
[3] *Ibid.*
[4] W. H. Bragg, Phil. Mag. *27*, 881 (1914).
[5] W. L. Bragg, R. W. James and C. H. Bosanquet, op. cit.

respect to the face will not equal their angle of reflection. The difference in measured reflecting power illustrated in these two tables has been explained as due to the fact that the X-rays will be relatively less absorbed in the crystal when the reflection angle is greater than the angle of incidence. It is considered that if the crystal face is sufficiently true so that

TABLE III

ORIENTATION	INTENSITY		
	Second order	Fourth order	Sixth order
Right hand rotation	100 units	21.3	5.08
Left hand rotation	116.6 .	21.8	5.08

this difference is not great, the mean of the intensities in the two orientations can be taken to be practically that of the correct intensity of reflection. It will further be noted from the data of Tables I to III that with both this last effect and also with the changes in intensity that result from grinding, the intensity variations are great at small angles of reflection but nearly vanish in the higher orders.

The problems of intensity measurement introduced by differences in the physical state of the reflecting faces are largely eliminated by studying the internal reflections obtained by transmitting the X-rays through thin sections of the crystal. It may well be that the errors of absorption arising from this transmission method can be more accurately corrected than can specifications be laid down for obtaining significant intensity measurements from developed faces.

There are various procedures [1] which may be followed in mapping out the reflection from a crystal face using the spectrometer. The one to be used in any particular instance will depend essentially upon the information which it is expected to supply. For a general survey that is intended to ascertain the number and approximate positions of the reflections from a crystal face it is convenient to bind the crystal table and ionization chamber together so that the latter will move at twice the angular velocity of the former. In this way the crystal face will always be in the correct position to reflect X-rays into the chamber; once the zero setting has been made, it is necessary only to move the ionization chamber slowly over the desired angular range to obtain all the reflections which the face can give within that region.

When the positions of the reflections from a particular crystal face have been found and it is desired to study their relative intensities, the following course may be taken. The arm joining the crystal table and ionization chamber should be disconnected so that each can have an inde-

[1] W. H. and W. L. Bragg, op. cit.; W. L. Bragg, R. W. James and C. H. Bosanquet, op. cit.

pendent movement. The chamber is then clamped at the angular position necessary to receive the maximum effect for the reflection under investigation. The crystal should then be rotated about its position θ (corresponding to the 2θ of the ionization chamber) for some distance upon either side of the observed intensity peak and the intensities of reflection plotted against the angular position of the crystal. In making these measurements the exact angular position of the crystal is not of value and it is sufficient simply to move the crystal slowly at a constant angular velocity, recording the electroscope readings at regular intervals. The shape of the peak of this curve will depend upon the perfection of the crystal under examination. If it is a very good one, such as the diamond or magnesium oxide, the peak will be sharp; on the other hand should the crystal be poor, the alkali halides for instance, the peak is often so flat that it spreads out over the better part of a degree. In all cases it is evident that the maximum observed intensity cannot be taken as a measure of the intensity of a particular reflection. Some reflected "white radiation" and some scattered X-rays will enter the ionization chamber at the same time as the characteristic radiation producing the reflection peaks. The amount of the extraneous ionization due to these causes can be obtained from measurements of the intensity of reflection on either side of spectrum lines.

It frequently happens that the effective reflecting face is not at the center of rotation of the crystal table. In such a case the data will not fit accurately into the equation $n\lambda = 2d_{hkl} \sin \theta_n$. This disagreement can be removed with the aid of the correction[1]

$$\tan \theta_0 = \frac{e \sin \theta_f - f \sin \theta_e}{e \cos \theta_f - f \cos \theta_e}$$

where $2\theta_0$ is the "true" zero position of the ionization chamber and $2\theta_f$ and $2\theta_e$ are the chamber angles of reflections in the fth and eth orders respectively.

The X-ray spectrometer has found extensive use in the study of the wave lengths and other properties of X-rays. For instance in such measurements of intensity as are involved in the study of the white radiation at different wave lengths and different voltages and with different materials as targets, or in investigations of the absorption of X-rays, spectrometric methods are the only ones capable of any accuracy. For these and similar purposes refinements of apparatus and of technique have been introduced; but they have not been taken advantage of in making any considerable number of the observations now useful for crystal analysis.

[1] C. L. Burdick and J. H. Ellis, J. Am. Chem. Soc. *39*, 2518 (1917); R. G. Dickinson, ibid. *42*, 85 (1920).

Spectrometric observations can be made not only upon large crystals but upon ones with faces down to about one millimeter in diameter. With such small crystal faces the surface to be exposed to the X-ray beam must be defined by a shield; otherwise relative intensities in the various orders of reflection will be different from those obtained from a face which is large enough to more than cover the incident beam.

From the preceding discussion it may be seen that if the necessary care is exercised in the preparation and mounting of a crystal an accurate determination can be made of the angles through which X-rays are reflected from its faces. Unless special precautions are taken, observed intensities of these reflections will, however, be different under changed conditions of experimentation, even from the same face. As yet, enough accurate observations have not been made so that a standard procedure for obtaining thoroughly reproducible intensity observations can be laid down. From what is known of the experimental difficulties of getting satisfactory intensity measurements from crystals it is necessary to conclude that practically all of the observations that now exist cannot be accepted as more than qualitatively correct. It has been emphasized (Chapter III) that the present lack of knowledge of the factors determining the intensity of scattering of X-rays by atoms does not permit of more than a qualitative use of even perfect experimental measurements in determining the positions of atoms within crystals. The uncertainty concerning the accuracy of the existing spectrometer observations combined with the theoretical limitations to their use make them the least reliable of all crystal structure data. Their value is still further lessened by the fact to be touched upon in more detail later (page 172) that reflections from other faces than the one directly under observation may often get into the spectrometer and give rise either to incorrect intensities or to totally false reflections.

These various elements tending to make uncertain the results of spectrometric observations can probably all be eliminated if enough care and precautionary measures are taken. When further experimental and theoretical advances have given them a precise value it is also probable that intensity measurements can be made definite and reproducible. At that time the precision spectrometer will perhaps again become the most valuable means of studying the atomic arrangement in crystals. When, however, the somewhat elaborate precautions that are necessary to insure reliable spectrometric data are contrasted with the comparative ease with which information equally valuable for crystal analysis can be obtained by the other available methods, its practical value at the present moment appears greatly lessened. It is of course true that if all the necessary precautions are taken data will be obtained with the spectrom-

eter that are as good as, but scarcely more useful than, the same information produced by the other methods of observing diffraction effects. If these assurances of reliability are not offered, spectrometric measurements from any but the simplest faces upon the simplest of crystals are worthless in crystal analysis.

Spectrometric Observations with White Radiation. — A procedure has recently been suggested [1] which utilizes white radiation rather than monochromatic X-rays. For this purpose the ionization chamber is fixed at some angle 2θ and the intensity of X-ray reflection mapped while the crystal is slowly rotated. As the crystal is thus turned, one after another of the planes in that zone which has its axis parallel to the axis of rotation

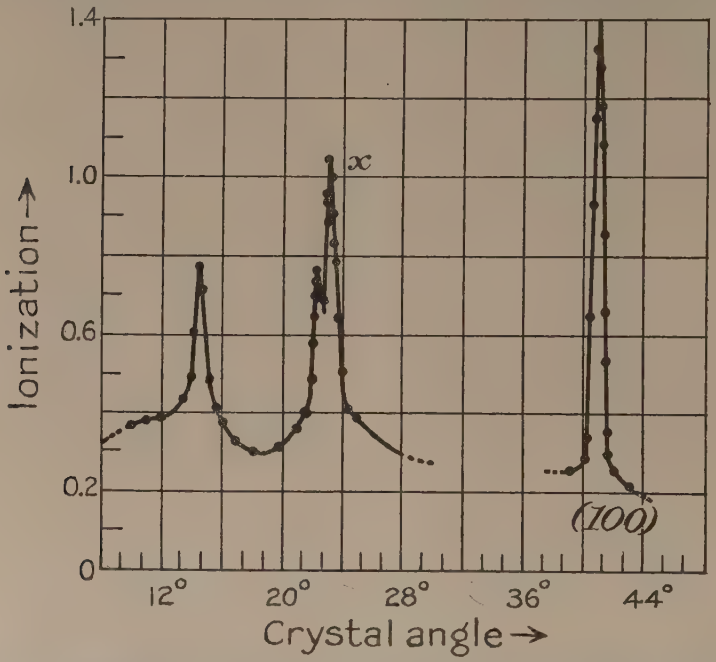


FIG. 116.—A crystal angle-ionization curve from a crystal of potassium iodide. A reflection from (100) is shown at the right; the so-called x-peak of the "anomalous diffraction" is shown in the center (after Clark and Duane).

will make an angle θ with the incident beam. In this position the planes will be capable of reflecting some wave length of X-rays and if such waves are present in the white radiation a reflection will be noted. Different portions of the continuous radiation will be effective for each plane. As a consequence of such measurements a curve resembling that of Figure 116 has been obtained by plotting the angular position of a crystal of KI

[1] G. L. Clark and W. Duane, Proc. Nat. Acad. Sci. *8*, 90 (1922).

against ionization. Knowing the original setting of the crystal it is possible to identify the planes giving rise to these peaks from measurements of the angles between them. It has been stated (page 68) that the intensity of white X-radiation produced at any one voltage is cut off sharply on the short wave length end of its spectrum at a point determined by the relation

$$V'e = h'c'/\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3 \text{ of Chapter II})$$

The wave lengths of the rays producing the peaks of Figure 116 can be established with the help of this equation by setting the crystal to give their maximum of reflection and then steadily lowering the voltage impressed upon the tube until the ionization current suddenly vanishes. If any estimates of relative intensity from these data are to be used in crystal structure studies, this wave length determination must be made for each reflection peak.

Intensity comparisons between different reflections are made more complicated in this method than in monochromatic spectrometry by the fact that they are taking place in different wave lengths. Furthermore all of these reflections are from undeveloped faces and consequently are subject to different amounts of absorption. None of the usual limitations of spectrometry are avoided by this procedure and it does not appear to be especially well adapted to recording the usual data for crystal analysis.

Spectrometry with white radiation seems, however, to furnish the best way of studying the reflections characteristic of atoms in the reflecting crystal[1] (page 80). In ordinary spectrometry a reflection is recorded by moving the ionization chamber so that its angular deviation from the incident beam is always twice that of the reflecting crystal face. If this is done using the continuous radiation and a crystal composed of atoms none of which has a characteristic radiation within the region of the white rays, such a curve as that of Figure 58 will be obtained. If, on the other hand, one or more of the atoms of the crystal have their characteristic radiations within this range of wave lengths, then the appearance of these curves will be greatly altered. The ionization measured from the (010) face of cesium triiodide, both of the atoms of which have their K-series lines within the range of the incident white radiation, is shown in Figure 117. According to this curve there is a characteristic effect which results in greatly exaggerated reflections at wave lengths corresponding to those of lines in the K-radiation of cesium and of iodine. It will especially be observed that these characteristic reflections from the different

[1] G. L. Clark and W. Duane, Proc. Nat. Acad. Sci. *9*, 126 (1923).

atoms do not necessarily occur together but are to be found in separate orders. This suggests that the phenomena offer the chance of producing a selective diffraction and interference from separate kinds of atoms constituting a crystal. Such data obviously will prove of great assistance in the analysis of many crystals.

The phenomena[1] of "anomalous diffraction" have been observed while using white X-rays in spectrometry. It has been reported that when a crystal with atoms giving characteristic radiation within the limits of the white region is used, not only are reflections from different

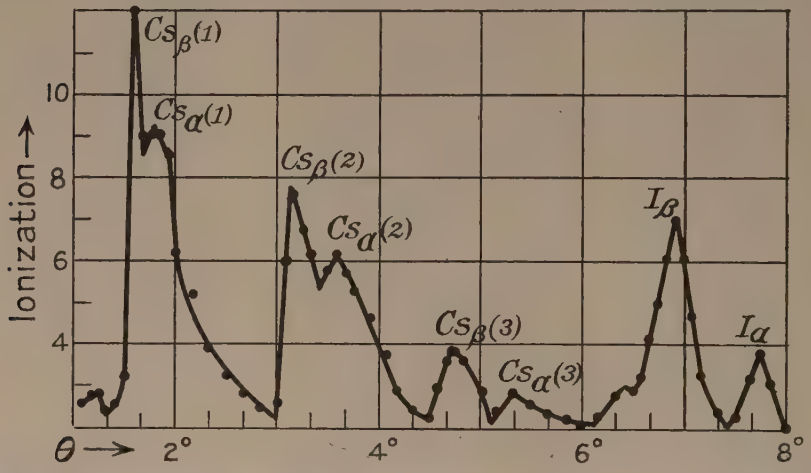


FIG. 117.—The intensity curve of X-ray reflection from a (010) face of CsI_3 showing the peaks characteristic of cesium and iodine atoms (after Clark and Duane).

planes registered as they come into position one by one but one or more additional peaks may appear. As yet this effect has been observed only with crystals of potassium iodide. From their wave lengths these so-called x-peaks seem to be characteristic of these atoms but they cannot be considered as reflections from any possible crystal planes. It is not yet determined whether they are definite properties of perfect potassium iodide crystals or whether, like the hazy effects commonly found upon Laue photographs of this[2] and other crystals,[3] they probably arise from crystal imperfections of some sort. Certain of their properties, notably their gradual disappearance as the incident beam is made increasingly parallel (see page 147), suggest that they may be causally related to crystal imperfections.

[1] G. L. Clark and W. Duane, Proc. Nat. Acad. Sci. *8*, 90 (1922); *9*, 131 (1923).
[2] R. W. G. Wyckoff, Am. J. Sci. *6*, 277 (1923).
[3] R. G. Dickinson, J. Am. Chem. Soc. *45*, 958 (1923); Phys. Rev. *22*, 199 (1923).

Spectrographic Methods

Spectrographic methods differ from those of spectrometry in the use of a photographic plate rather than the ionization chamber as an indicating device. A small portion of an X-ray spectrum can be photographed simply by employing a somewhat divergent beam and putting a photographic plate in the position of the chamber slit of a spectrometer. This spectrum may be badly distorted, however, if the crystal is poorly constructed. Its definition will be greatly improved and at the same time a complete record of the reflections from all possible planes will be obtained by rotating the crystal during the exposure [1] back and forth over a prescribed angular range.

Apparatus. A crude form of spectrograph is shown in Figure 118. X-rays pass through the variable lead slits S_1 and S_2 and strike the reflecting crystal mounted upon a rotating crystal holder at C. It is customary

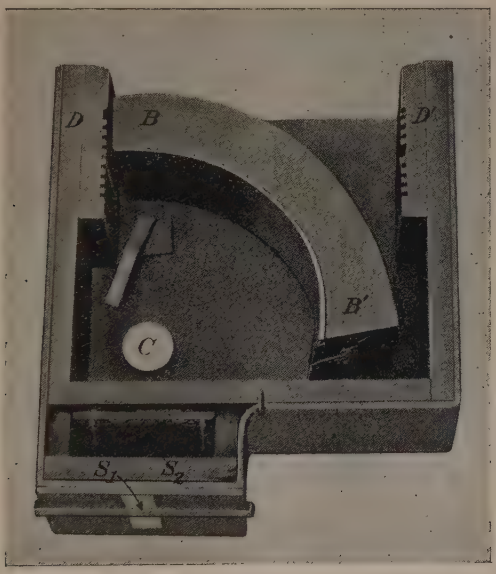


FIG. 118.—A simple form of X-ray spectograph for use in crystal analysis.

in accurate spectrographic observations for crystal analysis to make a photograph from the crystal under investigation and one from a standard crystal (usually calcite or rock salt) on the same plate. The crystal holder consequently must consist of a table and a templet for mounting these two crystals (in wax). Such a crystal holder will be illustrated at a later point. Unless a very large extent of spectrum is to be examined at one

[1] M. de Broglie, Compt. rend. *157*, 924 (1913).

time sharp enough lines will be obtained upon a photographic plate mounted at DD′. For extreme spectral ranges film in a hemi-cylindrical holder (BB′) should be substituted. If X-ray film rather than plate is used, it may be backed with intensifying screen to cut down the requisite time of exposure; but estimations of relative intensities upon the resulting photograph do not necessarily correspond to those made upon an unaided photographic emulsion.

During the course of an exposure the crystal should be moved back and forth over its prescribed path with a constant angular velocity. This can be done with sufficient accuracy by the simple cam arrangement shown in Figure 119. A form of the cam itself is shown under the base

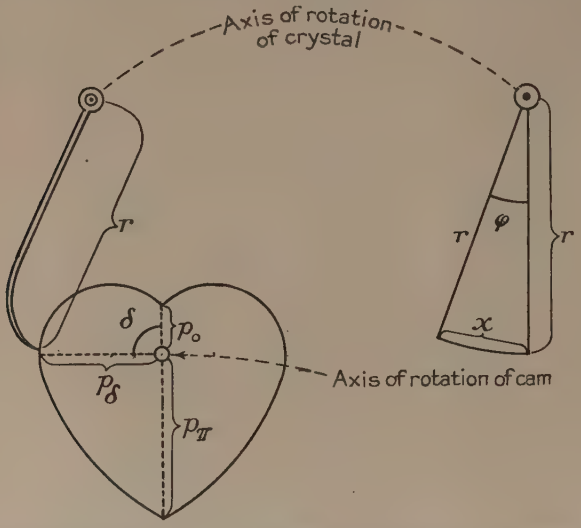


FIG. 119.—The essential parts of a cam designed to permit the uniform rotation of a reflecting crystal back and forth over any desired angular range. The cam itself is shown in Fig. 81.

of the instrument of Figure 81. Its dimensions for any desired angle of rotation ϕ can be obtained as follows. Expressing the angles in radian measure

$$x = \phi \times r = (p_\pi - p_0)$$

where r, the effective length of the rotation arm, and p_0, the smallest radius of the cam, may have any convenient lengths. A constant angular velocity of rotation of the crystal will result from a constant rotation of the cam if the latter is so constructed that

$$p_\delta = (p_\pi - p_0)\frac{\delta}{\pi} + p_0$$

where δ is chosen positively and negatively from 0 to π. For the best attainable results this cam should be driven by a small constant-speed motor; but the time of exposure for most crystals is so long that this speed regulation is unnecessary for all ordinary work. The motor should be geared down till the crystal will make one rotation in from one half to five minutes. It is convenient to have at least two cams for different angular rotations. One, which should give a rotation of 20° or 30°, is useful for a general mapping of the reflections for a crystal setting. With this wide angular motion the crystal is in a position to produce any one

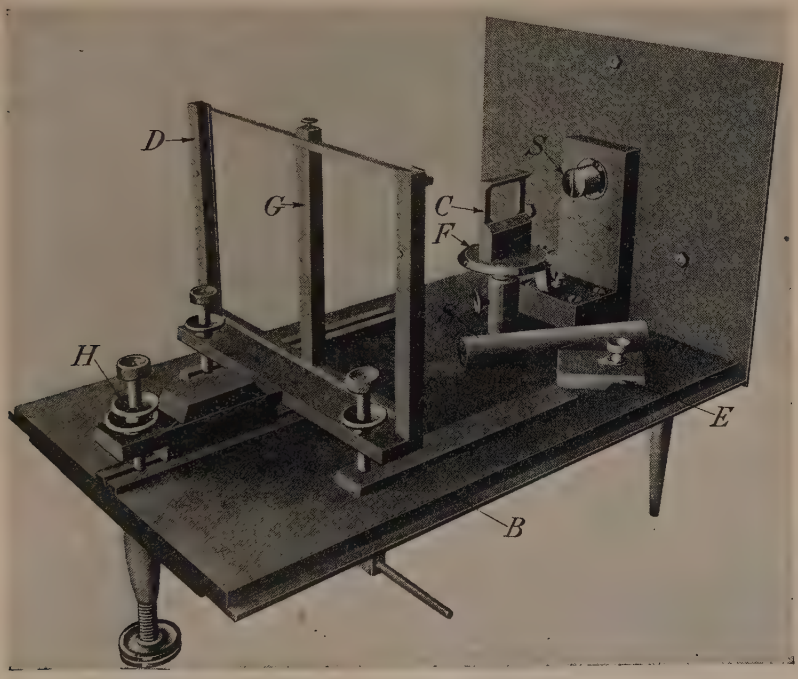


FIG. 120.—A more accurate form of X-ray spectrograph for use in crystal analysis.

reflection during only a small portion of its motion and consequently an exposure of several hours may be necessary to record a satisfactory spectrum. It frequently happens that a more intimate study of a small region of the spectrum is needed; a cam giving a rotation of 5°, or less, will then be required.

A more accurate form[1] of the spectrographic arrangement just described is shown in Figure 120. In this apparatus all parts are supported upon the cast metal base B. The slits are no longer adjustable but are built

[1] The instrument in essentially this form was designed by R. G. Dickinson and made by F. C. Henson.

as a series into a removable brass tube, S. The spectrograph may thus be equipped with several of these tubes of various slit widths. The crystal holder is shown at C; its templet for adjusting the crystal appears at E. With the aid of the attached graduated circle F, and various sizes of rotation cams, it is possible to make settings for reflections from any desired spectral region. The plate holder D can be made perpendicular to the incident X-rays with the tilting screw H and a brass T (not shown), one end of which is inserted for this purpose in place of the slit tube. The

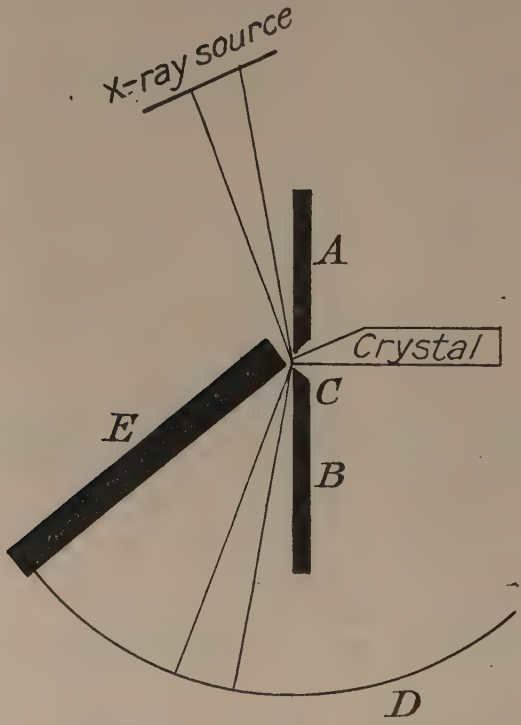


FIG. 121.—The essentials of one kind of "slit-less" spectrograph.

removable metal block G cuts out the directly transmitted beam of X-rays. Since all accurate measurements with this instrument are comparison observations against calcite or some other standard crystal, there is no need of measuring with precision the distance from the crystal to the photographic plate. This distance can be approximately determined with an auxiliary scale fastened upon the instrument. Its most convenient value is either five or ten centimeters, the latter being employed for accurate spacing measurements. Laue photographs also can be prepared with this same instrument by replacing the set of linear slits by a series

of pin-holes and putting the section of crystal either directly over the last of these or in a suitable goniometric holder replacing C of Figure 120.

For other purposes such as the study of the X-ray spectra of different elements, much more elaborate spectrographs than these have been described and used. This last one, however, in spite of its simplicity, furnishes data which are as accurate as any now attainable in crystal analysis.

"Slit-less" Spectrographs. — Other types [1] of spectrographs have been devised which do not avail themselves of parallel, or approximately

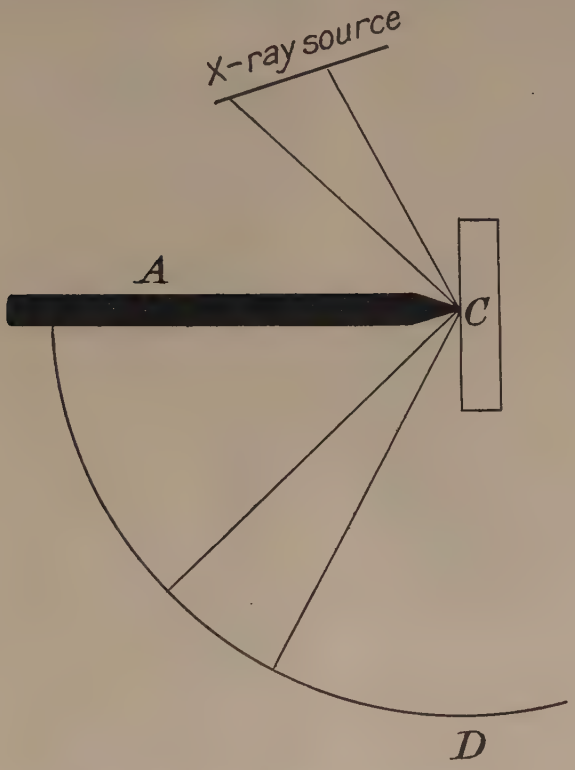


FIG. 122.—The "wedge" spectrograph.

parallel, X-rays. Their distinguishing feature is thus the absence of any system of slits. If an X-ray beam (Figure 121) is incident at various angles upon the small portion of crystal face C exposed through the lead screens A and B, a spectrum of the source will be produced upon a film at D. The lead baffle E protects the film from direct radiation. In the usual

[1] H. Seemann, Ann. d. Physik *49*, 470 (1916); *51*, 391 (1916); Physikal. Z. *18*, 242 (1917); *20*, 51 (1919).

type of X-ray tube the focal spot from which the rays originate is not large. It is therefore necessary to move the tube, or more conveniently the spectrograph, if more than a small portion of the spectrum is to be recorded. This form of instrument offers two distinct advantages. In

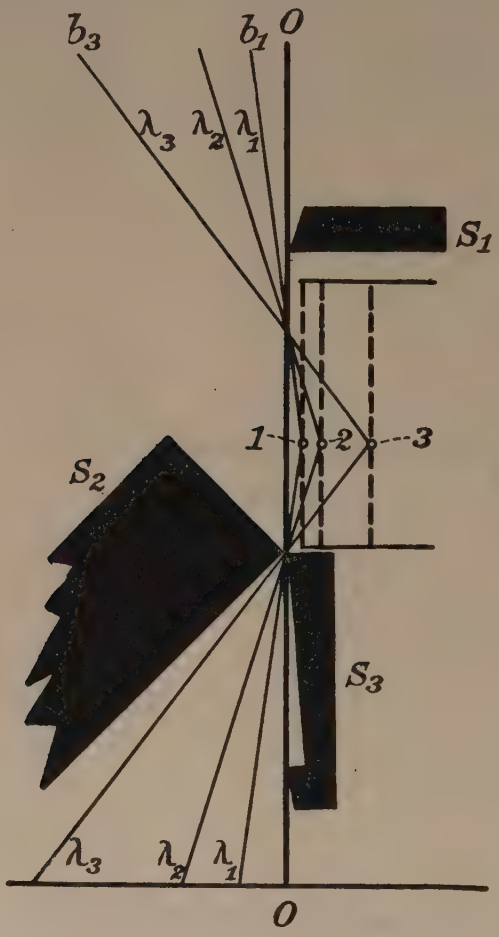


FIG. 123.—Another arrangement for "slit-less" spectrography.

the first place very small single crystals can be employed. Perhaps more important is the fact that since parallel radiation is not desired, it is not only possible but advantageous to bring the spectrograph very close to the target and thereby receive much more radiation from the tube. A variation of this experimental arrangement is shown in Figure 122. A wedge, A, of lead or other heavily absorbing material is pressed against

the reflecting face of the crystal C and serves both to define the position of reflection and to cut off direct radiation from the target. The spectrum lines obtained in this manner are usually wider and not so sharp as those from a slit spectrograph. It is, however, a property of these lines to be cut off abruptly on the long wave length side by the wedge and wave length measurements can be made using this boundary. One of the difficulties of these methods lies in establishing the position of zero deflection upon the film. A method of doing this for a somewhat different arrangement is shown in Figure 123. The crystal is mounted in front of the slit, S_2S_3, instead of forming a part of it. As the tube moves back and forth it successively comes into the positions necessary to reflect waves of different lengths (λ, λ_1, λ_2, etc.). If the crystal is stationary the reflections of these wave lengths which reach the plate will come from different parts of the crystal face; hence a large face must be used if a considerable spectral range is to be recorded. If, however, the crystal itself has a motion from position 1 to position 3 as the target moves from b_1 to b_3, the reflection point remains constant on the crystal face. In this way a small specimen may be employed. The zero position is sharply defined at O by the action of the three slits.

These additional spectrographic methods have not yet been much used in crystal analysis. Nevertheless they seem to be better for some purposes than the ordinary spectrometric and spectrographic procedures and a comparative study of their values in crystal analysis should sometime be made.

The Interpretation of Spectrum Photographs

The photograph of Figure 124 is obtained by reflecting molybdenum K-radiation from a (100) face of a crystal of sodium chloride which is rotating through an angle of about 30°. The central spectrum, P, with its path perpendicular to the undeviated slit image is the reflection from this face and is called the *principal spectrum*. During the motion of the crystal other atomic planes are brought one by one into position for reflection. The spectra from these other planes are inclined at various angles to the principal one; they are called *secondary spectra*.[1] Under certain conditions even the principal spectrum may not be produced by a single face. Thus if a crystal is so mounted that the axis of a zone which contains the principal reflecting face is parallel to the axis of rotation, various planes of this zone will be brought during rotation into positions to reflect along the line of the principal spectrum.

The indices of planes contributing to the principal spectrum can be immediately deduced if the orientation of the crystal is known. By

[1] See for instance H. Seemann, Physikal. Z. *20*, 169 (1919).

tracing the paths described by different planes during the crystal rotation the secondary spectral reflections can be identified. This is done [1] with sufficient accuracy by using the gnomonic rotation net in the following manner. Since the crystal orientation is completely known it is possible to plot in the usual fashion the gnomonic projections of all atomic planes at any one point of the rotation (conveniently chosen at one end or the middle of the path of the crystal).[2] As the crystal moves back and forth

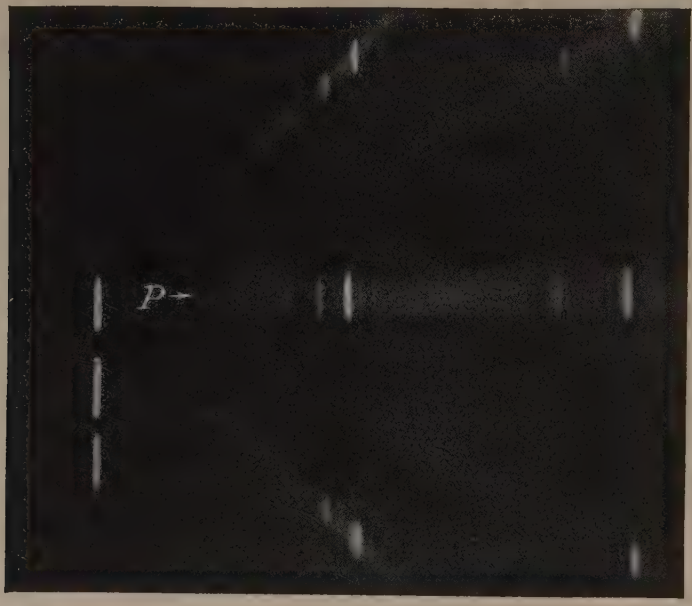


FIG. 124.—The K-lines of molybdenum reflected from a crystal of rock-salt (NaCl) set with a four-fold axis parallel to the axis of rotation and with the (100) face giving the principal spectrum.

the projections of these planes will travel over hyperbolic paths which can be marked out by a rotation with the net. For this rotation the net will be so placed that the projection of the plane producing the principal spectrum travels along the line PC″ of Figures 102 and 103. The gnomonic projections of planes in the positions for reflection are prepared by projecting some aspect of their spectra (the K-α line is convenient) with the gnomonic ruler. The procedure to be followed does not differ from

[1] R. W. G. Wyckoff, Am. J. Sci. *4*, 193 (1922). Detailed analytical treatments of these secondary spectra, usually under the name of "fibre diagrams" (see page 406) have been given in numerous papers by M. Polanyi, H. Mark, K. Weissenberg and others. Other methods have been discussed by E. Schiebold, Zeit. f. Physik *9*, 180 (1922) and by N. Uspenski and S. Konobejewski, Zeit. f. Physik *16*, 215 (1923).

[2] The necessary procedure has been described on page 134.

that described for Laue photgraphs. The projection of a reflecting plane made in this way must lie upon one of the hyperbolic paths already traced. The correctness of the resulting index assignment should be checked by a direct application of the customary equation

$$n\lambda = 2d_{hkl} \sin \theta_n$$

The essentials of this analysis will be clear from the following treatment of a very simple photograph of sodium chloride (Figure 124). For its preparation the crystal was mounted so that the axis of rotation was parallel to a four-fold symmetry axis and it turned back and forth through 30° starting from a position of parallelism between the X-ray beam and a cube face (Figure 125). The index field for this initial position is the

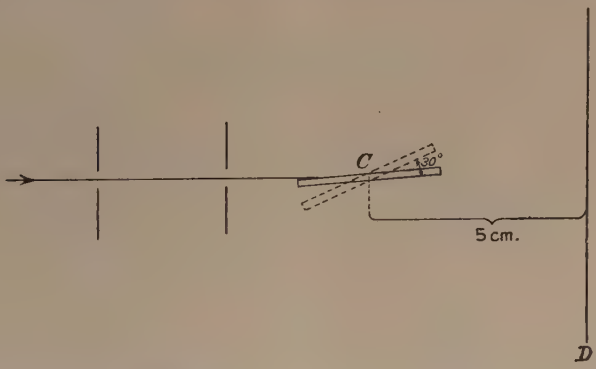


FIG. 125.—During the preparation of the spectrum of Fig. 124 the crystal had the motion indicated by C of this figure.

symmetrical one of Figure 104. As the crystal is rotated projections of some of the simpler atomic planes travel over the paths illustrated in Figure 126. The gnomonic projections of the reflections in the photograph, as obtained with the gnomonic ruler, are shown by black dots. The identification of the reflecting planes by determining upon which hyperbolas their projections lie is tested by the application of the equation

$$n\lambda = \frac{2a_0}{\sqrt{h^2 + k^2 + l^2}} \sin \theta_n \quad . \ . \ . \quad \text{(16a of Chapter III)}$$

to measurements upon the photographic plate (Table IV).

This same process will identify the secondary spectra upon photographs more rich in spectra and less symmetrical. In many such cases this analysis is a lengthy task. In fact it is usually more economical of time to determine as few secondary reflections as possible: data from

TABLE IV

Cube Face Reflection Spectrum of NaCl. Crystal — Plate Distance = 5 cm. a_0 = 5.628A° as measured from the principal spectrum. λ for K — α of molybdenum = 0.712A°.

(1) Spectrum (Figure 126)	(2) Center distance of K — α line	(3) Indices according to Figure 126	(4) d_{hkl}	(5) $\sin\theta$ (calc. from (2))	(6) $n\lambda$ (calc. from (4) and (5))	(7) (6) ÷ (0.712) = n
1	1.89 cm.	110	3.970A°	.180	1.434	2.01
2	3.28	210	2.510	.286	1.436	2.01
3	2.82	100	5.628	.255	2.870	4.03
4	1.31	100	5.628	.128	1.432	2.00
5	3.28	$2\bar{1}0$			1.436	2.01
6	1.89	$1\bar{1}0$			1.434	2.01

NOTE: The systematic error in these measurements which makes the quantities in column (7) always greater than whole numbers arises from the fact that the crystal-to-plate distance was not exactly five centimeters.

complicated planes are then more easily deduced from ordinary Laue photographs.

If a thin section is prepared from a crystal composed of not too heavy (intensely absorbing) atoms, an excellent spectrum photograph can be

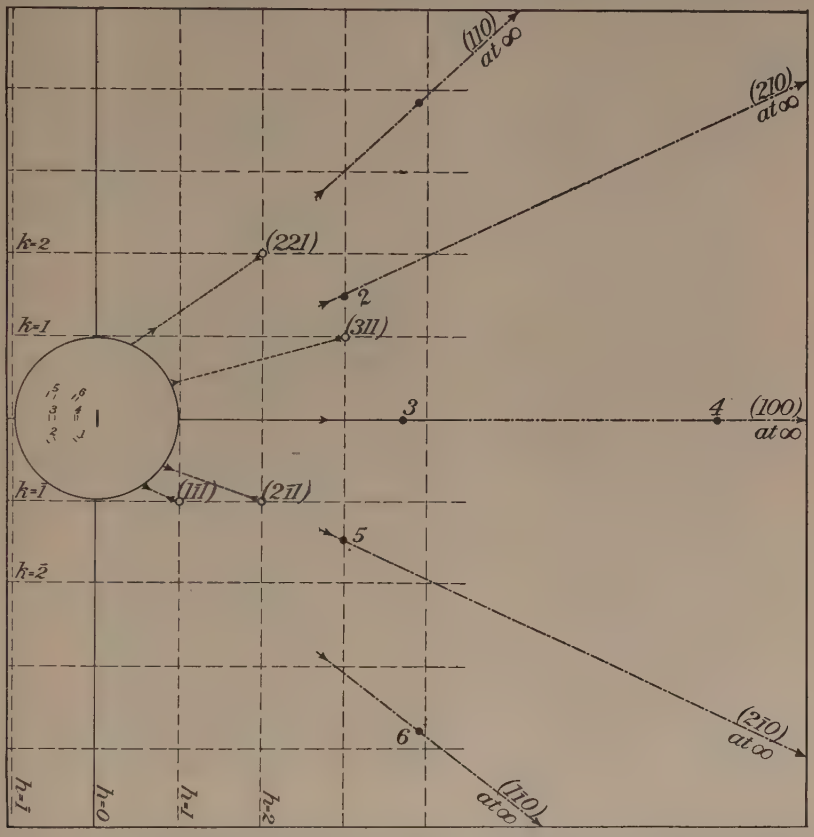


FIG. 126.—The gnomonic projection of the spectrum of Fig. 124 as used for the identification of its secondary spectra. The black circles are the gnomonic projections of the observed reflections of the K-α lines (of Mo). The paths, during the 30° rotation, of the projections of the planes which prove to be reflecting these rays are shown by the dot-and-dash lines. The projections of the paths of a few other planes (marked by open circles) are given by the dotted lines. A tracing of Fig. 124 appears in the center.

obtained by transmitting the X-rays through the section (as in Laue photography). With this experimental arrangement, the planes producing the various secondary spectra are more easily identified [1] by superimposing

[1] E. Schiebold in F. Rinne, Einführung in die Kristallographische Formenlehre, u. s. w. p. 199 (1919).

directly upon the reflection spectrum a Laue photograph (Figure 127). This Laue photograph may be taken with the crystal occupying any position within the angular rotation range of the reflection spectrum; it is not convenient, however, to make it too unsymmetrical. If this dual exposure is made the Laue photograph should be rapidly analyzed in the usual fashion and the reflection planes directly identified from it. Such a photograph is readily prepared with the apparatus of Figure 120. After the spectrum has been made it is only necessary to replace the line slits

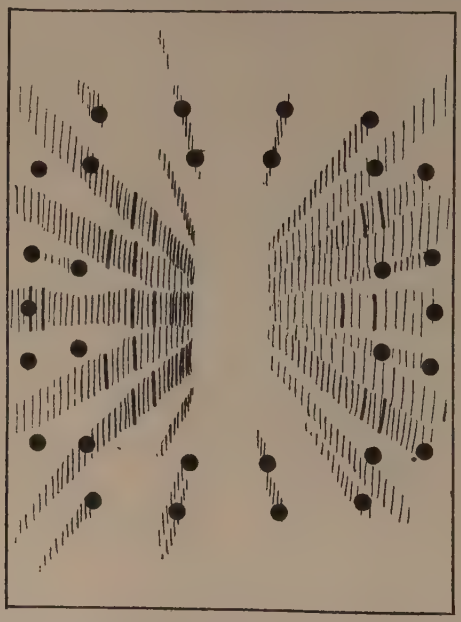


FIG. 127.—The superimposed Laue and spectrum photograph of rock salt (copied from F. Rinne).

with a tube of pin-holes and continue the exposure, now without rotation, for several minutes.

"Extraneous" Reflections. — With (1) a less simple principal reflecting plane, (2) less symmetrical orientation of the crystal for this plane, (3) more complicated crystal structure or (4) lower symmetry, the reflection photograph will be much more complicated than that of Figure 126. For instance the photograph from a (110) face of potassium aluminum [1] alum shows a large number of secondary spectra (Figure 128). This number will be even greater if the crystal is rotated (through an axis perpendicular to the principal reflecting face) so that the axis of rotation

[1] R. W. G. Wyckoff, Am. J. Sci. *5*, 209 (1923); Zeitsch. f. Kryst. *57*, 595 (1923).

is no longer parallel to a 4-fold symmetry axis. Such photographs illustrate one of the serious difficulties which may be encountered in the simple spectrometric examination of X-ray reflections: secondary spectra encroach upon the region of primary reflection. In spectrometric observations upon the principal spectrum the ionization chamber is moving at twice the angular velocity of the crystal and most of these reflections will

FIG. 128.—A photograph of the spectrum obtained by using the (110) face of potassium aluminum alum as the principal reflecting face for molybdenum K-radiation. The absence of observable odd order reflection from this plane is evident.

not of course be in correct positions ever to enter the chamber. This is not true, however, of all planes producing secondary spectra and as a consequence reflections from such planes may enter the ionization chamber and give rise either to false readings of intensity or to entirely new, and spurious, orders of reflection. That this has actually happened in the case of the (110) reflections from potassium aluminum alum seems certain when the photograph of Figure 128 is considered in connection with spectrometric observations [1] of Table V.

[1] L. Vegard u. H. Schjelderup, Ann. d. Physik *54*, 146 (1917).

TABLE V

Spectrometric Data upon the (110) Face of Potassium Aluminum Alum.

	Intensity in the nth order of reflection							
n = 1	2	3	4	5	6	7	8
9	100	38	30	0	41	0	20

It is clear that there is no photographic record of a third order reflection which the spectrometer readings indicate as more intense than the easily discernible fourth order. This source of error in the use of the spectrometer probably can be eliminated by making second observations of intensity after the crystal has been rotated several degrees about an axis normal to the reflecting face. All reflections which are not common to the two sets of measurements should then be discarded as spurious. If the relative intensity of reflection is changed by this rotation, the true intensity should be the minimum value measured after each of several such rotations. It is perhaps safer to determine the purity of the spectrum to be examined by a preliminary photograph. This can be done by placing a photographic plate directly in front of the slit of the ionization chamber.

Accurate Spacing Measurements for Crystal Analysis. — The exact dimensions of the unit cell of a crystal are most satisfactorily determined from spectrographic observations. For this reason the accurate measurement of interplanar spacings from the principal spectrum is of great importance in crystal analysis. The major sources of inaccuracy in data from reflection spectrum photographs of the type that have been described reside in uncertainties concerning (1) the distance from photographic plate to crystal face and (2) the zero from which the positions of spectrum lines upon the plate are to be measured. The first of these may be largely eliminated by calculating the crystal-to-plate distance from a standard comparison spectrum;[1] by measuring the separations of known lines upon the standard it is possible [2] to determine the zero position from this same spectrum. Figure 129 is a diagrammatic cross-section through the spectrograph used in preparing a comparison spectrum. The line AB is the trace of the photographic plate; C is the trace of the principal reflecting faces of the two crystals. The points a″, b″, c″ . . . f″ are spectrum lines from the standard crystal and O is the correct position of zero deviation. The point O′ is any arbitrarily chosen zero point of reference: thus it is the zero of the comparator (or ruler) with which the positions of the spectrum lines are read. Since the standard spectrum is well known and its con-

[1] R. W. G. Wyckoff, J. Am. Chem. Soc. *42*, 1100 (1920).
[2] R. W. G. Wyckoff and H. E. Merwin, unpublished data.

stants assumed to be correct, the angles of deviation (2θ) for all reflections are exactly determined. From this information the distance from crystal to plate, r, can be calculated from the data for two reflections a'' and b'' by writing

$$\frac{O'b'' - O'a''}{\tan 2\theta_{b''} - \tan 2\theta_{a''}} = r.$$

Measurements upon different pairs of lines will yield several determinations of r; from these an average value may be chosen as the distance from the crystal to the photographic plate. Each of these distances Oa'', Ob'' . . . etc., calculated through this average r, leads in turn (through

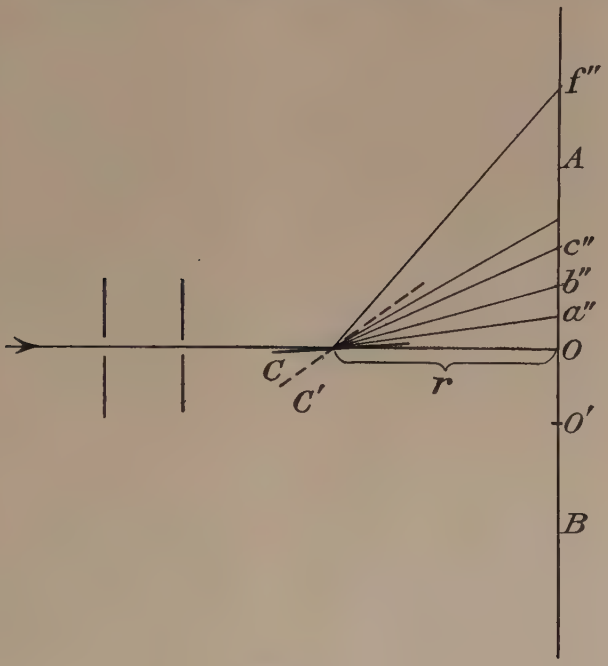


Fig. 129.

the relation $O'f'' - Of'' = OO'$) to a determination of the undeviated zero position. Once the crystal-to-plate distance and the zero position are known from the standard spectrum, their application to the measurements upon the unknown spectrum will lead directly to the spacing d_{hkl} of the unknown crystal through the equation $n\lambda = 2\, d_{hkl} \sin\theta_n$ and the known values of wave lengths.

This method of calculation is illustrated by some data (Tables VI and VII) drawn from a comparison reflection photograph in which the (100)

TABLE VI. DATA FROM A (100) REFLECTION FROM CALCITE AS USED AS STANDARD IN A COMPARISON PHOTOGRAPH WITH IRON DOLOMITE (SEE FIGURE 129).

Line (Figure 129)	K-line of Mo	O'f''	tan 2 $\theta_{f''}$	Of'' (from aver. r)	O'f''–Of'' (zero position)
a''	α (4)	131.8 mm	0.51220	50.48 mm.	81.32 mm.
b''	β (4)	125.3	.44637	43.99	81.31
c''	α (2)	104.9	.23946	23.60	81.30
d''	β (2)	102.2	.21184	20.88	81.32

Line (Figure 129)	$\left(\frac{\tan 2\theta_{a''}}{\tan 2\theta_{f''}}\right)$	O'a'' – O'f''	$\left(\frac{\tan 2\theta_{b''}}{\tan 2\theta_{f''}}\right)$	O'b'' – O'f''	r
c''	0.27274	26.9 mm.	—	—	98.63 mm.
c''	—	—	0.20691	20.4 mm.	98.55
d''	0.30036	29.6	—	—	98.59
d''	—	—	0.23453	23.1	98.50

average = 98.56 mm.

TABLE VII. DATA FROM A (100) REFLECTION FROM A CRYSTAL OF IRON DOLOMITE; THE PHOTOGRAPH STANDARDIZED BY THE DATA OF TABLE VI.

K-line of Mo	O'f''	Of''	tan $2\theta_{f''}$	λ	d_{100}/n,	d_{100}/n
α (6)	159.1 mm.	77.79 mm.	0.78926	0.710A°	0.962A° × 3	= 2.886A°
α (4)	134.6	53.29	.54068	.710	1.447 × 2	= 2.894
β (4)	127.9	46.59	.47271	.631	1.441 × 2	= 2.882
α (2)	106.1	24.79	.25152	.710	2.889	= 2.889
β (2)	103.2	21.89	.22210	.631	2.894	= 2.894

average = 2.889A°

faces of calcite and an iron-bearing dolomite [1] produce the principal spectra.

Spectrometric and spectrographic data, in recording reflections from individual crystal faces, furnish information that is invaluable in crystal analysis. The spectrometer observations are potentially the more valuable because they offer the possibility of direct measurements of intensity relationships. It has been shown, however, that not only will it be a difficult matter to measure these intensities with certainty and accuracy but that they would not now be of great use in locating the atoms in crystals were they available. Measurements of position and approximate estimates of intensity are made much more rapidly and certainly by the photographic procedures than by ionization chamber methods. As a consequence spectrographic procedures are the more widely useful at the present stage of the development of crystal analysis.

[1] R. W. G. Wyckoff and H. E. Merwin, unpublished data.

Spectrum Measurements at Other than Room Temperatures.—Spectrometer observations [1] upon several crystals have been made at temperatures up to about 900°C. The furnace used for this purpose, a nichrome-wound alundum tube, has been described in detail. No spectrographic work has been carried out at elevated temperatures.

[1] I. Backhurst, Proc. Roy. Soc. A. *102*, 340 (1922). See also W. H. Bragg, Phil. Mag. *27*, 881 (1914).

Chapter VI. Powder Spectrometry and Spectroscopy

A diffraction pattern is obtained when a thin film of crystalline powder is substituted for the single crystal of an X-ray spectrograph. If the individual crystals of this powder are haphazardly oriented so that they make all possible angles with the incoming X-ray beam, all orders of reflection from all possible atomic planes, above a certain minimum spacing, have the chance to register themselves at one time. The spectrum lines which result from these reflections of monochromatic X-rays constitute a *powder photograph* (Figure 130). The principle underlying the

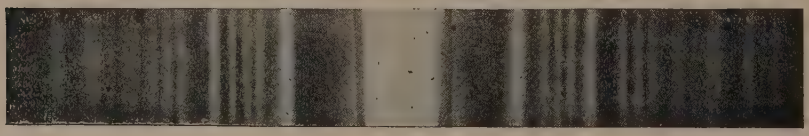


FIG. 130.—A powder photograph of calcite ($CaCO_3$). During exposure the film was bent around the arc ABD of Fig. 131. The position, B, of zero deflection is at the center of the photograph.

production of these photographs was brought forward as an early explanation of some Laue patterns from solid paraffin.[1] They became important, however, only when characteristic X-radiation was later used.[2]

If the powder is finely ground (to less than about 250 mesh) and its crystals have a completely unordered arrangement then a series of sharp diffraction images is obtained without rotation of the specimen. Such a powder pattern can be greatly simplified[3] by filtering the X-rays to render them essentially monochromatic (page 81). Any one line is composed of reflections from only a few particles of the powder; consequently more energy is required to produce one of these photographs than to record other X-ray diffraction phenomena. The outstanding advantage of powder diffraction methods obviously lies in their ability to treat the many crystalline materials which do not grow large single crystals.

[1] W. Friedrich, Physikal. Z. *14*, 317 (1913).
[2] P. Debye and P. Scherrer, Physikal. Z. *17*, 277 (1916); A. W. Hull, Phys. Rev. *10*, 661 (1917).
[3] A. W. Hull, op. cit.

The Preparation of Powder Photographs

Apparatus. — Numerous types of spectrographs have been devised for making powder photographs. Their essential details are shown in Figure 131. The X-rays from the target pass through the slits S_1-S_3 and, striking the crystalline powder placed at C, are diffracted and recorded upon a photographic film mounted along ABD. The powder may be most conveniently mounted, either as a rod or a thin film, at C, on the axis of the

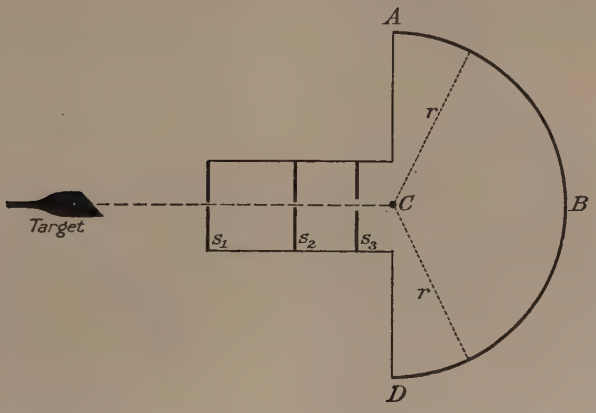


FIG. 131.—The essential parts of a powder spectrograph.

cylindrical surface ABD. The slit system consists of a series of either pinhole or line slits. With the former the diffraction pattern is a series of curved bands. The straight and parallel lines (the ends may be curved) resulting from the use of linear slits are more favorable to accurate measurements (Figure 130). The width of the slits will depend upon the degree of definition that is desired in the photographs. It is essential to have a third slit (S_3) to cut off the rays diffracted by the second slit; otherwise a diffraction pattern of the metal of this slit will be superimposed upon the lines of the crystalline powder.

A photograph of a powder spectrograph of the type [1] just described is shown in Figure 132. The slit system is contained within the draw tube S, the sample being placed directly over the inmost slit. The two outer slits are six centimeters apart, of variable width and are made from millimeter sheet gold. The third slit, S_3, set three centimeters behind the second gold slit, is made of one-eighth inch brass heavily plated with gold and tapered on the inside to the edges of the slit-opening (which for ordinary

[1] A somewhat similar instrument has been described by A. W. Hull, Phys. Rev. *17*, 571 (1921). The spectrograph of this figure was developed largely through the efforts of E. W. Posnjak and C. J. Ksanda.

measurements may have a width of two and one half millimeters). The body of the spectrograph and the cover (F) are copper castings, the front is a brass plate faced on the outside with sheet lead. The back, milled to form a hemicylindrical surface with its axis passing through the crystal position, may have an intensifying screen fastened permanently to it. The use of this screen is optional. It undoubtedly shortens somewhat the necessary times of exposure but its effectiveness at low intensities is not great and through too great an intensification of the strong lines, the pattern will be faultily recorded. In making an exposure the sensitive duplitized film is put into direct contact with the screen, if one is used, and covered on the inside with a sheet of black paper to exclude any

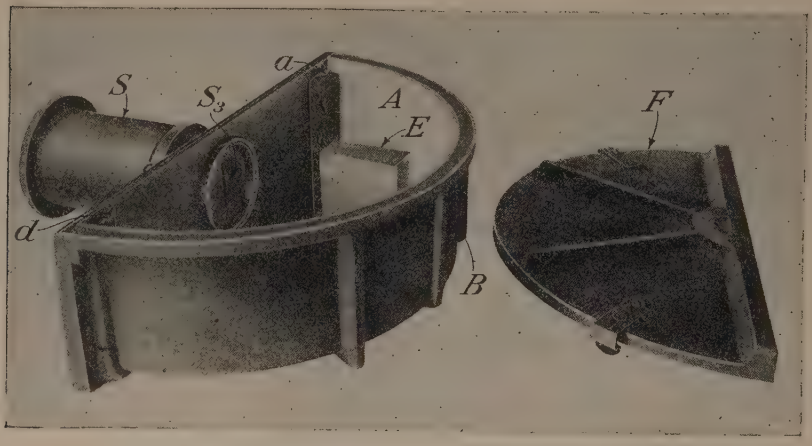


FIG. 132.—A photograph of a powder spectrograph.

small light leaks. The film is held in place by the two sliding clips a and d. The inverted sliding V (E of Figure 132), open at the two ends and faced on the sides with thin lead, serves the double purpose of helping to hold the film in place and of protecting the film from the X-rays scattered when the directly transmitted beam strikes the film. The filtering screen (of zirconium, in the form of the dioxide, if molybdenum K-radiation is employed) may be placed either in front of the slit system S, or directly in front of the photographic film [1] or partly in one place and partly in the other. If only a small piece of screen is available it must be placed over the first slit. The best photographs are to be obtained, however, by using it just before the film, for in this position it not only absorbs practically all of the reflected radiation except the K-alpha lines but also most of the secondary radiations emitted by the crystalline powder. This secondary

[1] A. W. Hull, Phys. Rev. *17* 571 (1921).

radiation is very pronounced for crystals containing elements a little lighter than the target element; for instance there will be a large amount of scattered rays from crystals containing elements immediately lighter than zirconium, if molybdenum radiation is used. This radiation shows itself mainly as a general fogging of the film; for lighter elements near the target material this blackening may be so intense as completely to obliterate the true diffraction pattern. The only reason for not always placing the filter next to the film arises from the difficulty of making large enough pieces which will be uniform over their entire length. In many cases, especially where faint lines are sought or where there is a large amount of secondary radiation and satisfactory filters are not available, it is profitable to use two films instead of one. The instrument may be directed towards the target with the aid of a small opening (B); it is best placed so that the beam of X-rays used makes a small angle with the face of the target. It has been customary to make the radius of this sort of spectrograph either about 10 or about 20 centimeters. The one just described is of the smaller size. The strip of film required for it is 13.5 inches long and 2.5 inches wide. Good photographs of crystals of high symmetry can be produced with the powder either contained in a fine thin-walled glass tube or spread out into a film upon paper or with collodion as a binder. In dealing with strongly absorbing materials it has often been the practice to dilute the unknown powder with flour [1] or some other light material. Where these extraneous substances are non-crystalline, their general scattering is enough to obscure faint diffraction lines; those like flour which are crystalline themselves produce many faint reflections that may interfere with the ones due to the unknown powder. For these reasons the only thoroughly satisfactory sample would be a compressed rod of powder; for strongly absorbing materials these rods must be so fine, however, that their preparation is difficult. Another procedure which may be useful consists in coating a silk fiber with powder held together by a small quantity of binder.[2]

Spectrographs of the type just described are convenient and accurate to use if the number of exposures to be made simultaneously and with the same tube does not exceed two or three. When many powder photographs are desired, as in any routine check and analytical uses to which the method might be put, this set-up would prove totally inadequate. An apparatus primarily fitted for such purposes has been described.[3] With it as many as 15 photographs can be made at one time. A reproduction of a photograph of the complete outfit is shown in Figure 133.

[1] W. P. Davey, Gen. Elect. Rev. *25*, 565 (1922); J. Opt. Soc. Am. *5*, 479 (1921).
[2] H. Küstner, Physikal. Z. *23*, 257 (1922).
[3] W. P. Davey, op. cit.

The essential parts of the spectrographs are arranged as in the preceding instrument. The X-ray tube stands vertical within the metal cylinder (A) into which the 15 slit systems are permanently built. The first two slits, one of glass and the other of brass, serve to limit the X-ray beam; the second brass slit is a wide one designed to cut off rays scattered by the second defining slit. The holder for specimen and film is of the quadrant, as opposed to the hemi-cylindrical, type. It opens in the back for the

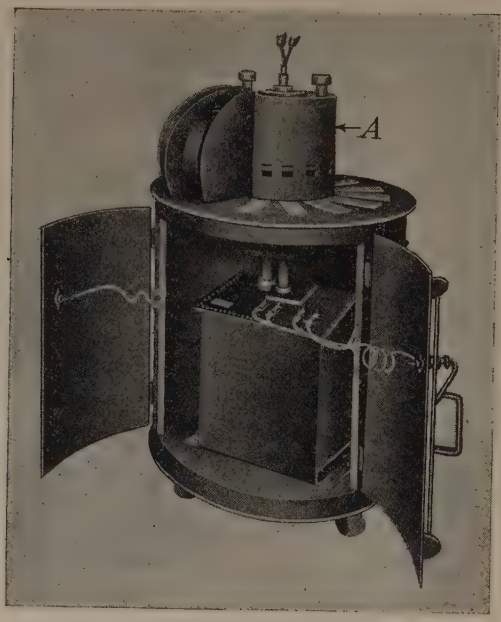


FIG. 133.—A multiple spectrographic outfit (after Davey).

insertion of the film which is behind the filter and is followed by a strip of intensifying screen and a brass strip to hold them in place. The undeviated beam passes through varying thicknesses of copper so that some portion of the zero line will always have an intensity comparable with that of the diffraction lines of the resulting photograph. A series of molybdenum steps place on the end of each film a scale for approximate intensity comparisons. These film holders are also divided so that comparison photographs can be obtained by filling half the length of a specimen tube with one substance and the rest with another.

Powder photographs could of course be obtained with such a spectrograph as the one described for use with single crystals (Figures 118 and 120). This instrument, however, would not prove of advantage for the preparation of powder photographs except those of substances, such as

pieces of metal, which could not be used as powders. In these cases it is possible to obtain a photograph, if reflections from very large angles are not needed, by mounting the face to be examined as if it were the face of a single crystal and rotating the crystal holder through a small angle during the exposure.

Powder reflections have also been observed with the ionization chamber by putting a sheet of powder in the position of the crystal face in the X-ray

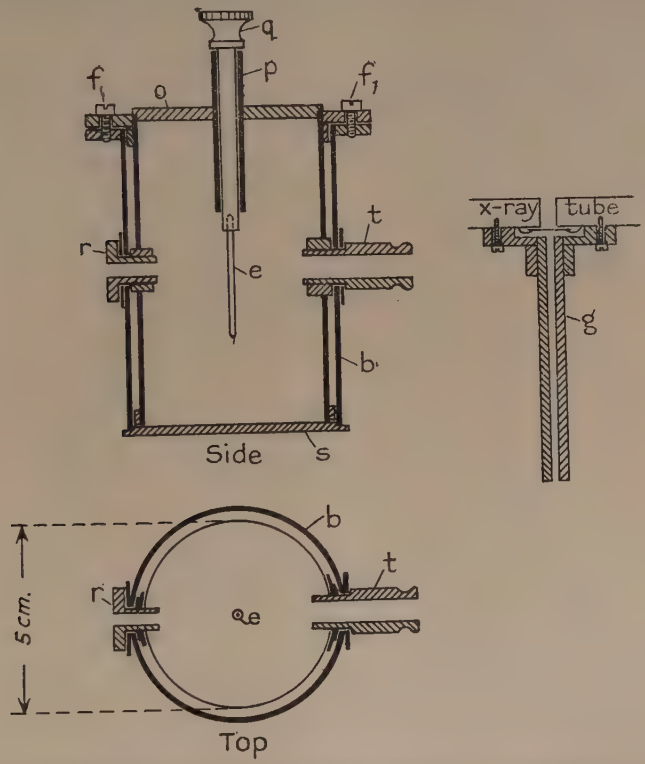


FIG. 134.—The details of a small holocylindrical powder spectrograph (after Pauli)

spectrometer.[1] As yet this procedure has not been used for the complete elucidation of any structures.

A small cylindrical spectrograph [2] similar to the apparatus originally used in preparing powder photographs [3] is shown in Figure 134. This form of instrument is usually employed with a metal X-ray tube;[4] in

[1] W. H. Bragg, Proc. Phys. Soc. London *33*, 222 (1921).
[2] O. Pauli, Zeitsch. f. Kryst. *56*, 591 (1921–22).
[3] P. Debye and P. Scherrer, op. cit.
[4] R. von Traubenberg, Physikal. Z. *18*, 241 (1917); A. Hadding, Zeitsch. f. Physik *3*, 369 (1920).

this way the diffracting powder can be brought so close to the source of X-rays that exposures of less than two hours are sufficient. For many purposes such a short exposure is of great advantage in spite of the difficulties accompanying measurements intended to be as accurate as those possible with the larger instruments. The pin-hole slit system in the form of a lead-lined brass tube (g) can be screwed directly into the side of the X-ray tube. The spectrograph proper consists of two concentric cylinders. The outer one (b) of brass is attached to a brass base (s). The inner cylinder has its sides cut away to furnish windows through which the reflected beams may pass. In this form it consists essentially of an upper and lower ring of metal joined only in the region of the entrance tube (t) and the exit tube (r). The windows are completely covered with black paper. A cover (o) contains a collar (p) for the rod (q) into which the tube of powder (e) is mounted. The photographic film punched with suitable holes for the entrance and exit tubes is placed between these two

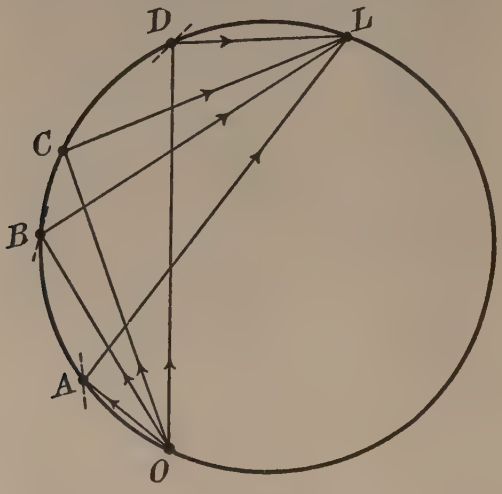


FIG. 135.

coaxial cylinders which then may be fastened together by the screws f and f_1 and the tubes (t) and (r). This wrapping the film entirely around the inside of the cylinder permits the registration of reflections at great angles — if they have sufficient intensity. After the specimen (e) has been mounted in the axis of this spectrograph, the latter is set for the exposure by inserting the slit (g) into the tube (t).

In Figure 135 the angles OAL = OBL = OCL =, etc. They are all supplements of the glancing angles of reflections from crystals located at the points A, B, C, etc. Consequently if O were the source of a diver-

gent beam, X-rays of a wave length λ would be focused upon some point L by reflection from appropriately oriented crystals lying upon the circumference of the circle OAB. Thus it happens that a powder photograph could be prepared by having a powder strewn over a portion of this circular arc.[1] The cross-section of a spectrograph[2] built upon this principle is shown in Figure 136. Reflections from the different atomic planes in the crystalline powder spread upon the inside surface of AC register themselves upon the photographic film wrapped around the inside of the cylinder

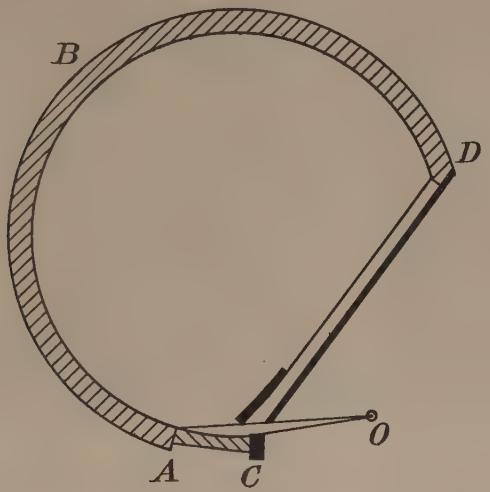


FIG. 136.—A cross-section through a "focusing" powder spectrograph.

ABD. A fine-focus tube gives a point source (O) of X-rays. The focal spot of the target of this tube must lie on the circumference of ABD if sharp diffraction lines are to be obtained. This arrangement brings the source of X-rays very close to the diffracting powder and thereby offers the chance of producing photographs with very short exposure times.

The different "slit-less" methods of X-ray spectrography described in the preceding chapter can also be adapted to the preparation of powder photographs. It is, however, a serious objection to their use for determining the structures of crystals that the intensities of the diffraction lines cannot be taken as proportional to the intensities of reflections from the corresponding crystal planes. A more extended description of these procedures is not justified because thus far they have found little application to powder photography. Shorter times of exposure seem to be possible from their use and thus they may prove valuable in technical practice and

[1] H. Seemann, Ann. d. Physik *59*, 455 (1919); H. Bohlin, ibid. *61*, 421 (1920).
[2] H. Bohlin, op. cit.

in high and low temperature observations, where exposures of a few minutes will be either imperative or of great usefulness.

It is probable that an impartial experimental comparison of all of these ways of producing powder photographs would result in apparatus and technique superior to those now existing.

Powder Spectrography at Other than Room Temperatures. — On several occasions powder photographs have been made at elevated temperatures. When the crystalline specimen is metal which can be made into fine wire,[1] it can be heated electrically. Accurate temperature control has not been attempted with crystalline salts. The experimental arrangement used in the few rough observations upon crystalline salts has not been described.[2] A few observations[3] have been made at low temperatures by blowing a stream[4] of air, evaporated from liquid air, over the powder specimen. The temperature was regulated with an auxiliary electric heater.

The Interpretation of Powder Photographs

It has been said that in the haphazard distribution of small crystals which constitutes a powder specimen, some crystals will be in position to reflect X-rays of a given wave length from all atomic planes having a spacing greater than a certain minimum value (see below).

If for the present certain minor corrections required for the greatest accuracy are neglected, the distance on the photograph from a reflection line to the central undeviated image divided by the distance from the powder to the photographic film gives 2θ, twice the reflection angle of the X-ray beam. If the powder reflection is recorded upon a plate this quotient would be $\tan 2\theta$. Since the wave length λ of the rays producing the powder reflection is known and $\sin\theta$ can be calculated from this determination of 2θ, the ratio of the spacing of the planes producing each powder line to the order n of reflection, d_{hkl}/n, is given by the following rearrangement of the equation $n\lambda = 2\, d_{hkl} \sin\theta_n$:

$$\frac{d_{hkl}}{n} = \frac{\lambda}{2 \sin\theta_n} \qquad \text{(24)}$$

Since $\sin\theta$ has a maximum value of unity it is obvious from this equation that no reflection is possible from planes for which $d_{hkl}/n < \frac{\lambda}{2}$.

The problem of determining the indices (hkl) from the spacings that are calculated with expression (24) varies in complexity with the sym-

[1] A. Westgren, Zeitsch. physikal. Chem. *98*, 181 (1921).
[2] G. Bartlett and I. Langmuir, J. Am. Chem. Soc. *43*, 84 (1921).
[3] L. W. McKeehan, Proc. Nat. Acad. Sci. *8*, 254 (1922).
[4] P. P. Cioffi and L. S. Taylor, J. Opt. Soc. Am. *6*, 906 (1922).

metry of the crystalline powder and with the amount of information available from sources other than the powder photographs. Several cases requiring different treatments present themselves.

When both the Symmetry and the Size of the Unit Cell are Known. — The simplest case arises when both a spectral reflection from a single crystal face and knowledge of the crystallographic properties of the material are available. With these facts at hand the length of side, a_0, of a possible unit cell can be deduced and the spacings of all other planes calculated with the appropriate form of equation (15) of Chapter III:

$$d_{hkl} = \frac{a_0}{\sqrt{F(hkl;\ abc;\ \alpha\beta\gamma)}} \quad . \quad . \quad . \quad . \quad (15)$$

By comparing these spacings with the ones measured on the powder photograph [using (24)], the planes giving rise to each of the observed reflections can be identified. This procedure will be illustrated by assigning indices to the strong lines in the powder photograph of cubic magnesium oxide. The molybdenum K-alpha line with an effective wave length of 0.710A° was used in making this photograph (Figure 137 *a* and *b*). A

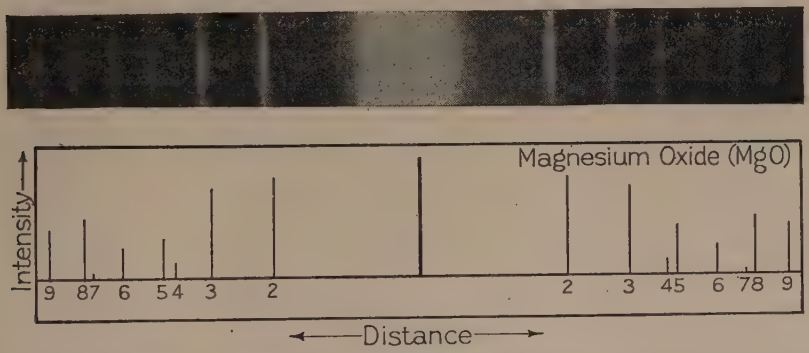


Fig. 137*a*.—A powder photograph of magnesium oxide (MgO) taken with the spectrograph of Fig. 132.

Fig. 137*b*.—A tracing of the powder photograph of MgO reproduced in Fig. 137*a*. The lengths of the traced lines are proportional to their intensities in the original photograph. The appended numbers are those of column (1) of Table II.

reflection photograph from the cube face of a single crystal of magnesium oxide, reduced in the manner described for iron dolomite (page 175), yields $d_{100}/n = 2.10$A°. The length of its unit cube, a_0, must be some integral multiple of this ratio, that is, 2.10A°, or 4.20A°, or 6.30A°, etc., depending upon the value of n. Assuming in turn each of these dimensions, the spacings of other simple planes can be found from the equation

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \quad . \quad . \quad . \quad . \quad (15a \text{ of Chapter III.})$$

The resulting absolute spacings of various planes, if n = 1, 2, 3 and 4, are shown in Table I. The distance from the crystal to the film in the

TABLE I. SPACINGS OF REFLECTING PLANES FOR MgO FOR VARIOUS VALUES OF n IF THE CUBE FACE REFLECTION, d_{100}/n, = 2.10A°

INDICES OF PLANE	n = 1	n = 2	n = 3	n = 4
100(1)	2.100A°	4.200A°	6.30A°	8.40A°
100(2)	1.050	2.100	3.15	4.20
100(3)	.700	1.400	2.10	2.80
100(4)	.525	1.050	1.57	2.10
100(5)	.420	.840	1.26	1.68
100(6)	.350	.700	1.05	1.40
110(1)	1.480	2.960	4.44	5.92
110(2)	.741	1.480	2.22	2.96
110(3)	.494	.988	1.48	1.98
110(4)	.370	.741	1.11	1.48
111(1)	1.210	2.420	3.64	4.85
111(2)	.606	1.210	1.82	2.42
111(3)	.404	.808	1.21	1.62
111(4)	.303	.606	.91	1.21
112(1)	.857	1.710	2.57	3.43
112(2)	.428	.857	1.28	1.71
113(1)	.632	1.260	1.90	2.53
113(2)	.316	.632	.95	1.26
120(1)	.937	1.870	2.81	3.75
120(2)	.468	.937	1.40	1.87
130(1)	.664	1.330	1.99	2.65
130(2)	.332	.664	.99	1.33
133(1)	.481	.962	1.44	1.92

spectrograph used in preparing this photograph was 10.81 cm.; the measured distances between corresponding lines on either side of the position of zero deflection are given in column (3) of Table II. The angle 2θ, in radian measure the ratio of one half the distances of column (3) into the crystal-to-film distance, is stated in column (4). Absolute spacings calculated from these data through expression (24) give column (5). A comparison of these spacings with those of Table I shows a fit between calculated and observed spacings if n is either two or four.[1] Crystallographically possible unit cubes which are in agreement with these powder results then have lengths of edge of 4.20A° and 8.40A°. The indices of the planes producing these reflections are the same for both unit cells; the orders of individual reflections referred to the larger unit are twice those of the reflections expressed in terms of the smaller cell.

[1] In this instance values of n = 1 and n = 3 could equally well have been eliminated by calculations of the mass associated with the corresponding unit cells (see page 202).

TABLE II. DATA FROM A POWDER PHOTOGRAPH OF MgO. CRYSTAL-TO-FILM DISTANCE = 10.81 cm.; $\lambda = 0.710$A°

(1) LINE (Fig. 137b)	(2) INTENSITY	(3) DISTANCE BETWEEN CORRESPONDING LINES	(4) 2θ	(5) d_{hkl}/n	(6) INDICES if n = 2
2	10	7.34 cm.	19°28′	2.10A°	100(2)
6	3	14.92	39°32′	1.05	100(4)
11	1	23.05	61° 6′	0.698	100(6)
3	9	10.47	27°43′	1.48	110(2)
10	½	21.60	57°14′	0.741	110(4)
1	2	6.34	16°48′	2.43	111(1)
5	5	12.88	34° 8′	1.21	111(2)
9	5	18.50	49° 2′	0.856	112(2)
4	2	12.28	32°32′	1.27	113(1)
13	¼	25.75	68°14′	0.633	113(2)
8	6	16.80	44°32′	0.937	120(2)
12	½	24.48	64°52′	0.662	130(2)
7	½	16.38	43°24′	0.960	133(1)

For cubic crystals the unit cells that are crystallographically possible can differ from one another only in the lengths of their edges. In crystals of lower symmetry the crystallographically possible units will have different shapes and may have different orientations. This will complicate a process of index assignment to powder lines which, however, is in principle the same as that just outlined for magnesium oxide. It should be emphasized that the unit cell, and its corresponding set of coördinate axes, thus used to give indices to reflecting planes, is only one of a number of possible units; referred to other units of different shapes, the indices of a reflecting plane will usually be different.

When only the Symmetry is Known. — A slightly modified procedure may be used if the symmetry properties of the powder are well known, but no single crystal is at hand to furnish a reflection measurement. This way of identifying powder lines will be illustrated with the powder measurements on magnesium oxide just recorded. Equation (16a) of Chapter III gives on rearrangement:

$$\frac{4a_0^2 \sin^2\theta}{\lambda^2} = (h^2 + k^2 + l^2)n^2 \quad . \; . \; . \; . \; (25).$$

The right hand side is always integral; all but $\sin^2\theta$ on the left is a constant for this photograph. Consequently the ratio of $\sin^2\theta$ for any two reflections will equal the ratio of two integers which, at least for the most conspicuous lines, probably will not be large numbers. From values of $(h^2 + k^2 + l^2)$ for various possible planes and from several of these ratios of squared sines of the reflection angles, the correct indices of the

planes producing the powder lines can be assigned after a short set of trials. Thus the sine-squares for the first five lines in the powder spectrum of magnesium oxide stand in the ratio of $\sin^2\theta_1 : \sin^2\theta_2 :$ etc. $= 0.02134:$

TABLE III. VALUES OF $(h^2 + k^2 + l^2)n^2$ FOR SOME SIMPLE PLANES IN A CUBIC CRYSTAL

INDICES	d_{hkl}/a_0	$(h^2 + k^2 + l^2)n^2$
100(1)	1.000	1
110(1)	.706	2
111(1)	.577	3
100(2)	.500	4
120(1)	.446	5
112(1)	.408	6
110(2)	.353	8
100(3)	.333	9
130(1)	.316	10
113(1)	.301	11
111(2)	.288	12

$0.02857 : 0.05734 : 0.07846 : 0.08613 = 3 : 4 : 8 : 11 : 12$ (very closely). Reference to Table III indicates that these five lines are reflections from planes having the indices 111(n = 1), 100(n = 2), 110(n = 2), 113(n = 1) and 111(n = 2). The correctness of this assignment is checked and the indices of the other reflections determined by calculating $(h^2 + k^2 + l^2)n^2$ for each observed reflection. The indices of reflections from crystals of less than cubic symmetry can be found in the same manner by using in place of (25) the suitable form of equation (16) of Chapter III. In these cases, however, the right hand term will no longer be integral. If the crystal system is cubic, hexagonal or tetragonal it frequently happens that the indices of reflecting planes can be ascertained more quickly with the aid of graphical charts [1] such as those shown in Figures 138 *a* and *b* and 139. These plots give the relative spacings of some simple planes for unit hexagonal and tetragonal cells having all possible axial ratios within their range. The spacings of planes in a cubic crystal will be found along the line c = 1 in the tetragonal chart. With this plot the indices of the magnesium oxide reflections of Figure 137 can be obtained in the following manner. The spacings, in Ångstrom units, of these reflections as calculated from the direct measurements upon the powder photograph are plotted upon the edge of a piece of paper following the logarithmic scale at the bottom of Figure 139. The axial ratio of a cubic crystal being unity, the paper scale thus prepared must be moved horizontally along the line of this axial ratio until there is coincidence between the curves of the

[1] A. W. Hull and W. P. Davey, Phys. Rev. *17*, 549 (1921).

plot and each observed spacing (Figure 140). The indices of the planes giving the powder lines may then be read off directly. Hexagonal and tetragonal crystals of known axial ratios are treated in precisely the same manner.

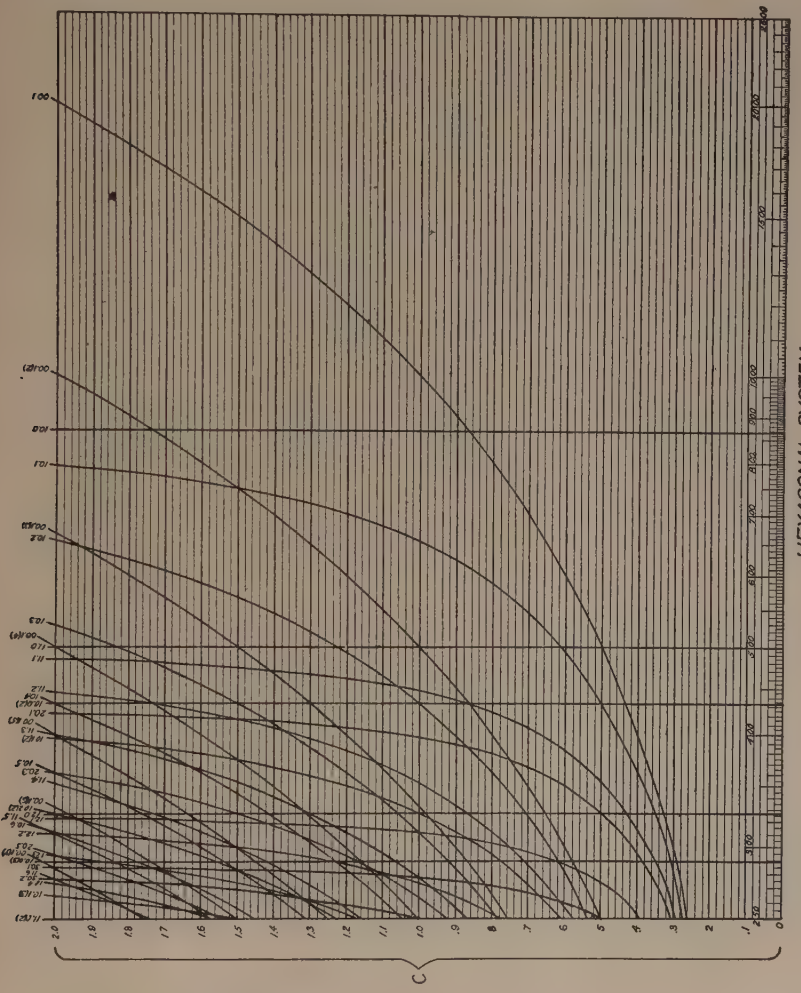


FIG. 138a.—A plot of the variation of the spacings of various *hexagonal* planes with the value of the axial ratio c. In this figure c lies between 0 and 2.0 (after Hull and Davey).

When the Symmetry is Incompletely Known. — The logarithmic record of spacings must be moved vertically as well as horizontally over the charts until a coincidence is discovered if the crystal under examination is either hexagonal or tetragonal but with an undetermined axial ratio. For instance moving the logarithmic plot of the strong lines of pyrrhotite over the face of Figure 138 shows (Figure 141) an agreement with the axial

ratios c : a = 0.82, 1.64, etc. On account of their more or less approximate character great care must be exercised in the application of these charts, particularly when, as in this last case, the crystallographic properties are not thoroughly established. It scarcely needs to be emphasized that

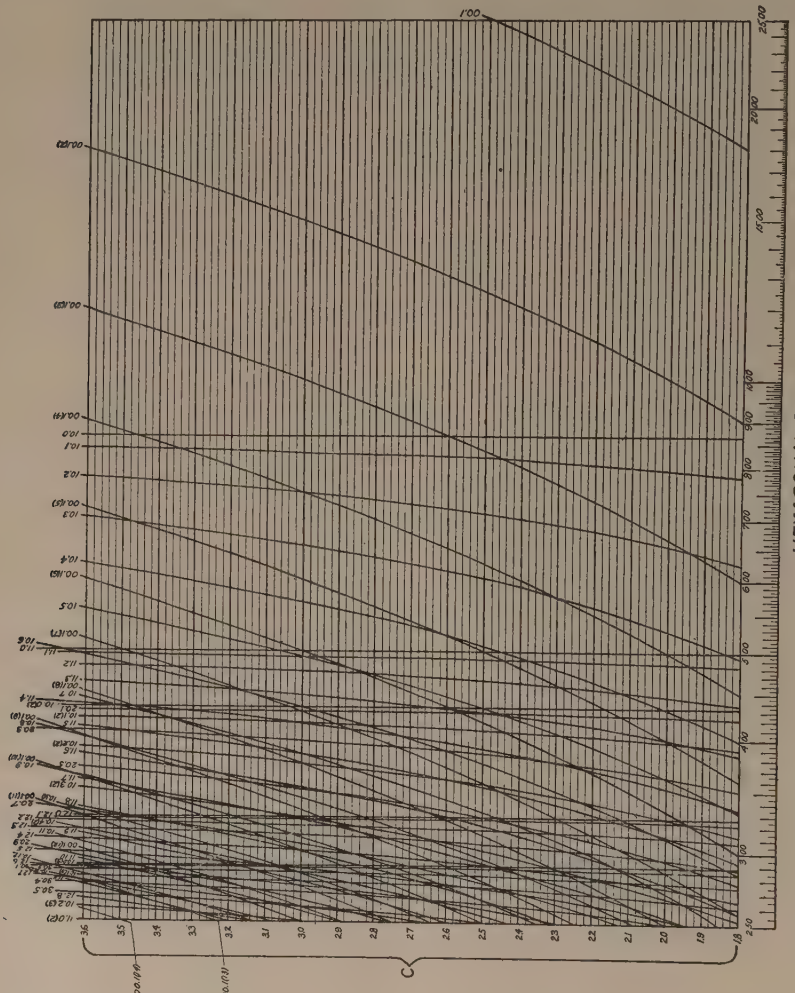


FIG. 138b.—A continuation of Fig. 138a in which c lies between 2.0 and 3.6 (after Hull and Davey).

except perhaps where reflections from very simple planes are concerned all assignments of indices should be checked by direct calculations of spacings. A purely analytical procedure [1] has also been suggested for

[1] A. Johnsen and O. Toeplitz, Physikal. Z. *12*, 47 (1918).

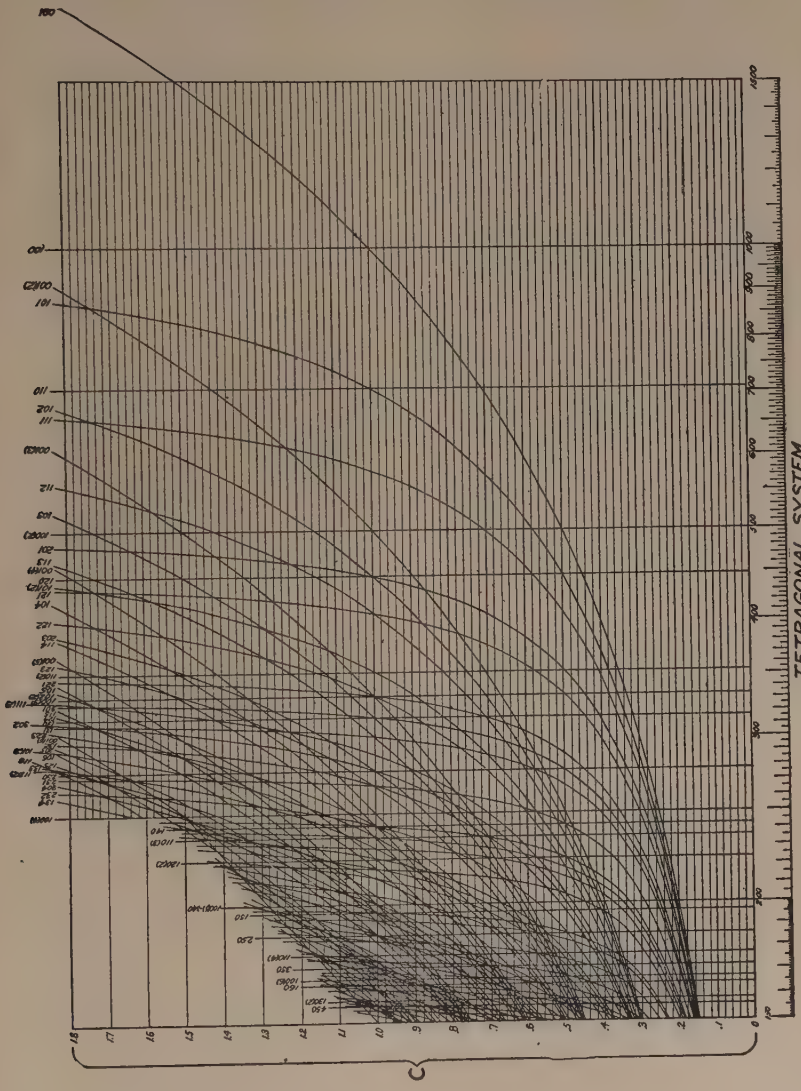


FIG. 139.—A plot of the variation of the spacings of various *tetragonal* planes with the value of the axial ratio c (after Hull and Davey).

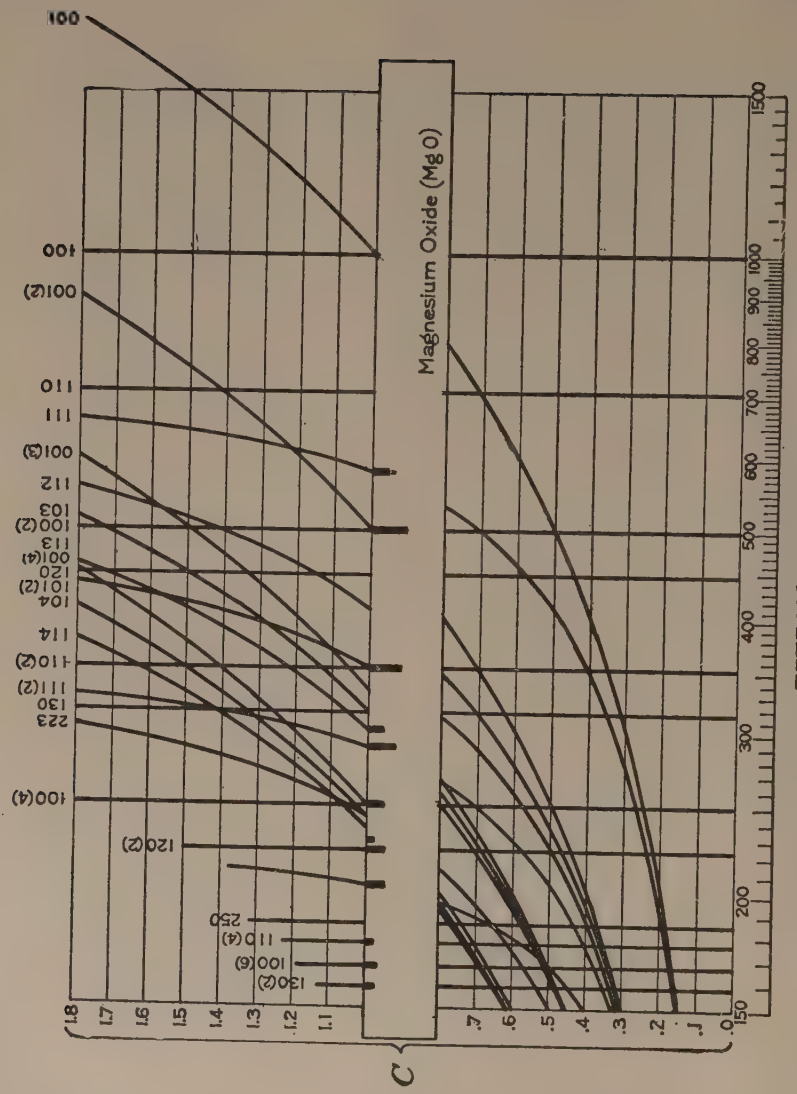


FIG. 140.—A figure showing the superposition upon the plot of Fig. 139 of the observed spacings (in a powder photograph) of magnesium oxide. The indices of these powder lines can be read immediately.

identifying reflecting planes in hexagonal and tetragonal crystals. This method has not been largely used as yet in crystal analysis.

It is not feasible to prepare charts for orthorhombic, monoclinic or triclinic crystals because of the greater number of variables that are

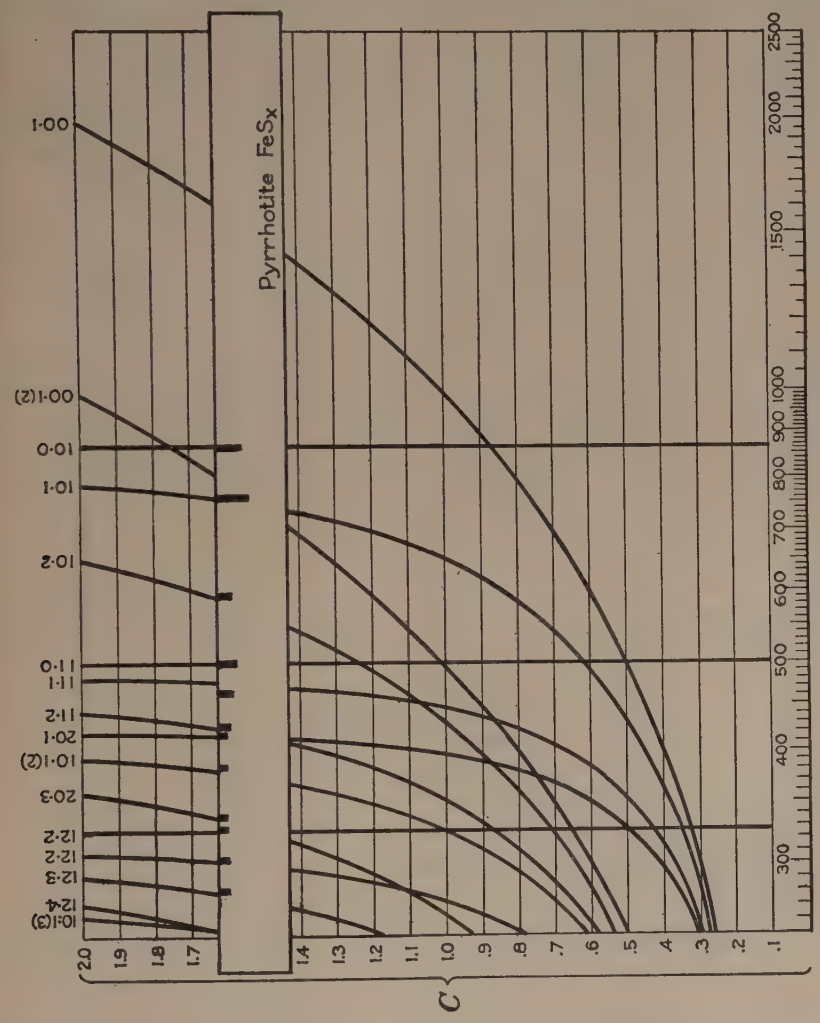


Fig. 141.—A figure showing a possible superposition upon the plot of Fig. 138a of the observed spacings (in a powder photograph) of pyrrhotite.

involved. An analytical process [1] has been devised, however, which is theoretically capable of establishing a possible unit cell for these crystals as well as for those of greater symmetry; but its application is so arduous a task that no genuine test of its usefulness has yet been made.

[1] C. Runge, Physikal. Z. *18*, 509 (1917).

Accurate Spacing Measurements. — In order to obtain any considerable accuracy from spacing measurements on powder photographs, certain precautions must be taken and corrections (or their equivalent) applied. In the first place it is not easy to get an accurate measure of the distance of the somewhat broad powder spectrum lines from the central undeviated slit image. If such a direct measurement of the angle of deviation of a line is to be made, as is the case if a quadrant spectrograph (page 182) is employed, the difficulty is lessened by inserting such a thickness of absorbing material in the path of the direct beam that the resulting photographic image has an intensity comparable with that of the reflected beams. This sort of absorbing screen should also be used in defining the zero beam for the various forms of "slit-less" spectrographs. Hemicylindrical and cylindrical instruments have the advantage that no determination of the position of zero deviation is necessary; measurement can be made between corresponding lines on either side of the zero. The other quantity required to establish the angle of reflection of powder lines is the crystal-to-film distance. An approximate measure of this can of course be made directly; a spectrograph is, however, best standardized by preparing a powder photograph of either sodium chloride or calcite (the two primary wavelength standards) under the same conditions that will subsequently be employed in examining unknown substances.

Calculations of spacings using the crystal-to-film distance obtained from such a standardization will not always yield results of great accuracy. If a rod of powder is used and the incident X-rays diverge after passing through the slit system the powder lines will be found farther from the position of zero deviation than would be the case with parallel X-rays.[1] An approximate correction for this can be introduced. The positions of reflection lines will likewise be influenced by the size and the absorptivity of the crystalline rod.[2] In Figure 142 AA′ is an incident beam of X-rays which on striking the tube of powder C gives rise to a reflection at the angle 2θ. If the crystalline material were completely transparent to X-rays the center of the reflected image would lie at C′ on the film E′F′. If the powder were opaque then reflection would take place only from a section of its surface and the spectrum line would be found at B′D′. Thus the reflection would appear to be shifted towards greater angles. Most crystal powders range between these limits and as a consequence their lines exhibit an apparent displacement. An approximate correction to allow for this shift has also been suggested. Conditions are simpler if a sheet of powder is used instead of a rod but the varying thickness of the film and the difficulties of holding it plane interfere with direct accurate measurements.

[1] O. Pauli, op. cit.
[2] Ibid.

In using the spectrograph of Figure 133 an attempt to allow for this absorption is made by mixing heavy absorbing powders with some light material such as flour.[1] A comparison photograph of sodium chloride and of this mixture is then prepared by filling one half of the specimen tube with sodium chloride and the rest with the mixture. The introduction of the foreign crystalline starch is a serious disadvantage, particularly in the study of crystals with low symmetry. A more satisfactory procedure is one which mixes the comparison powder (sodium chloride or calcite usually) directly with the powder under investigation.[2] This mixture

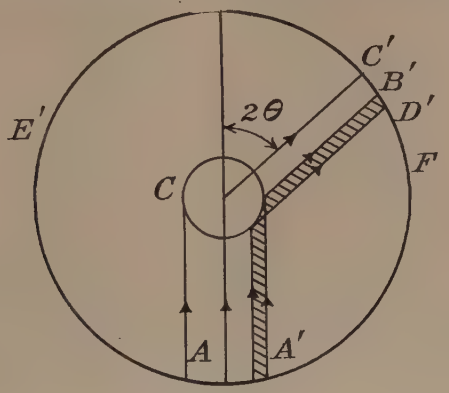


FIG. 142.

can then be formed into a sheet or put into a tube for photographing. Under these conditions the lines of the comparison standard are subjected to the same measure of absorption and apparent deviation as are those of the unknown. Consequently, if the standard lines are used to calibrate the film for a particular observation, the corrections which have been mentioned above are automatically cared for more accurately than by calculation. It is better to make identifications of reflecting planes upon an additional photograph of the pure unknown substance. This method of accurately determining the spacings of powder lines from a comparison photograph of sodium chloride and metallic iridium is illustrated by the data of Tables IV and V and Figure 143. The specimen was a film of iridium and sodium chloride in collodion. Column (2) of Table IV records the distances of the standard lines from the central undeviated image (as obtained by halving the separation of corresponding lines on either side of the zero); column (3) states the spacings, d_{hkl}, of these planes as calculated from equation (15a) and the known dimensions of the sodium

[1] W. P. Davey, op. cit.
[2] R. W. G. Wyckoff, Zeitsch. f. Kryst. *59*, 55 (1923).

chloride unit; and the last column gives the reflection angle θ as calculated from equation $n\lambda = 2\, d_{hkl} \sin \theta_n$. An average value of r, the distance from crystal to film (Figure 131) is obtained from the data of columns

Table IV. Sodium Chloride Data from a Comparison Powder Photograph of Iridium and Sodium Chloride

Plane	Distance (D) of Line from Zero Image	dhkl	θ (in radians)
100(2)	27.05 mm.	2.814A°	0.12649
110(2)	38.60	1.990	.17937
111(2)	47.40	1.625	.22027
100(4)	54.85	1.407	.25506
120(2)	61.65	1.258	.28597
112(2)	67.5	1.149	.31415
110(4)	78.7	0.9949	.36486
100(6), 122(2)	83.8	.9380	.38813
130(2)	88.4	.8899	.41035
132(2)	106.1	.7521	.49159

(2) and (4) and the relation $D = 2\, r\theta$ either by a simple averaging or probably better by applying the method of least squares.[1] For the Ir-NaCl experiment r is found in this way to be 107.76 mm. (data of Table IV). The application of this standardization to the lines of iridium gives the results shown in Table V. The measurements of column (2) divided

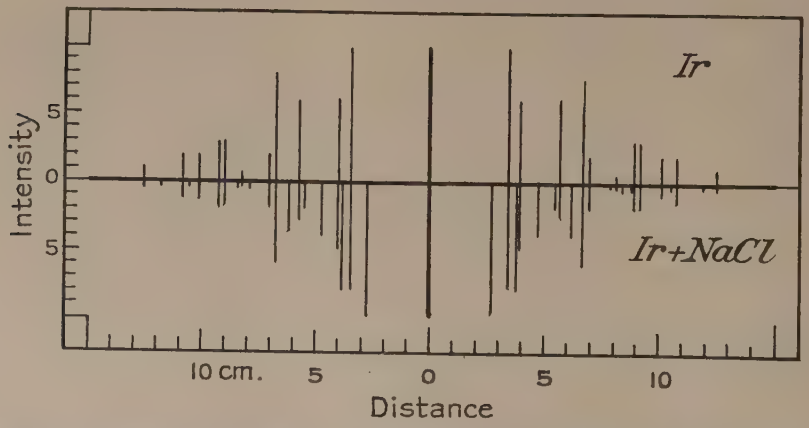


Fig. 143.—Tracings of the lines in a simple powder photograph of iridium (above) and in a comparison photograph of iridium mixed with sodium chloride. As usual the heights of the traced lines are proportional to their intensities upon the original film.

[1] Using this latter method the crystal-to-film distance r will be obtained from the expression $2r = \frac{\Sigma D\theta}{\Sigma \theta^2}$.

TABLE V. IRIDIUM DATA FROM THE COMPARISON PHOTOGRAPH OF TABLE IV

PLANE	DISTANCE (D) OF LINE FROM ZERO IMAGE	d_{hkl}	a_0
111(1)	34.7 mm.	2.214A°	3.835A°
100(2)	40.2	1.914	3.829
110(2)	57.05	1.357	3.838
113(1)	Omitted because practically coincident with 112(2) of NaCl		
111(2)	70.5	1.106	3.830
100(4)	82.3	0.9526	3.810
133(1)	89.9	.8762	3.819
120(2)	92.35	.8544	3.821
112(2)	102.0	.7788	3.816
111(3) } 115(1) }	108.6	.7352	3.820
110(4)	118.8	.6778	3.834
100(6) } 122(2) }	127.6	.6361	3.817
		Simple Mean =	3.824A°

by r yield values of 2θ which when applied in the equation $n\lambda = 2\, d_{hkl} \sin\theta_n$ lead to the spacing data of column (3) and to the dimensions of (4) after an identification of these lines by one of the procedures previously outlined. These values of a_0 from different lines suggest the accuracy that can be obtained from ordinary measurements on powder photographs; it is found, however, that the average dimensions calculated from different photographs agree rather more closely than data from individual lines would suggest.

The Intensity of Powder Reflections.—In the calculation of the relative intensities of powder reflections from a given arrangement of atoms, one factor in addition so those enumerated in expression (20) of Chapter III must be considered. In a haphazard distribution of crystalline particles equal numbers of the individual crystals will be inclined at all desired angles towards an incident X-ray beam and thus will be in a position to reflect X-rays from any possible crystal face. All planes having the same relative spacings give powder reflections in the same position and consequently the reflections from all of the faces of a crystal form are superimposed upon one another in the formation of a single powder spectrum line. If the crystal under examination has a center of symmetry then the intensity of a spectrum line contributed by the planes of a form will be equal to that calculated for a single plane by expression (20) multiplied by the number of planes in the form. If the crystal is not possessed of a center of symmetry the intensity of (20) must be multiplied by twice the number of planes in the form unless the form, taken by itself,

TABLE VI. VALUES OF j FOR REFLECTIONS FROM ALL FORMS IN ALL CLASSES OF CRYSTAL SYMMETRY

SYMMETRY	INDICES OF FORMS	j
I. Triclinic System		
1C, 1Ci	[hkl]	2
II. Monoclinic System		
2c	[hkl]	4
2C, 2Ci	[hk0] or [001]	2
III. Orthorhombic System		
2e	[hkl]	8
2D	[100], [010] or [001]	2
2Di	[0kl], [h0l] or [hk0]	4
IV. Tetragonal System		
4c	[hkl]	8
4C	[001]	2
4Ci	[hk0]	4
4d	[hkl]	16
4e	[001]	2
4D	[100] or [110]	4
4Di	[hk0], [0kl] or [hhl]	8
V. Cubic System		
T, Ti	[hkl]	24
	[100]	6
	[111]	8
	[0kl]	12
Te, O, Oi	[hkl]	48
	[100]	6
	[111]	8
	[110]	12
	[0kl] or [hhl]	24
VI. Hexagonal System (hexagonal indices used throughout)		
A. Rhombohedral Division		
3C, 3Ci	[hk·l]	6
	[00·1]	2
3e	[hk·l]	12
3D	[00·1]	2
3Di	[11·0] or [h$\bar{h}$·l]	6
B. Hexagonal Division		
6c	[hk·l]	12
6C	[00·1]	2
6Ci	[hk·0]	6
6d	[hk·l]	24
6e	[00·1]	2
6D	[11·0] or [1$\bar{1}$·0]	6
6Di	[hk·0], [hh·l] or [h$\bar{h}$·l]	12

has such a center. This arises from the fact, already mentioned in discussing the symmetry of Laue photographs (page 117) that since reflection must be imagined to take place from a series of internal atomic planes parallel to a crystal face, the same reflection is obtained from any face and from a parallel one on the opposite side of the crystal.

The intensity of powder reflection from the planes of a form (or of the two inverse forms if the crystal is without a center of symmetry) may consequently be written

$$I_{[hkl]} \propto j \times I_{(hkl)} = j \cdot (A^2 + B^2) \cdot \left(\frac{d_{hkl}}{n}\right)^{2.35} \quad . \quad . \quad . \quad . \quad (26)$$

where j equals either the number of planes in a form or twice that number. The values of j for all the forms of each of the 32 classes of symmetry can be immediately deduced from their indices (Table III of Chapter I); they are given in Table VI.

It scarcely needs to be emphasized that the lines in a powder photograph frequently are due to reflections from planes of more than one form. For example since the values of $(h^2 + k^2 + l^2)$, and consequently their spacings, are the same (in cubic crystals) for planes of the forms [341] and [501] their reflections will be exactly superimposed with the formation of a single spectrum line. In many more instances, especially with crystals of low symmetry, powder lines from different forms will not have identical positions but nevertheless will lie so close together that their separation is difficult.

As is the case with intensity observations upon other diffraction effects, practically all the existing measurements of lines in powder photographs have been visual estimations; the few photometered films are not of much greater value as indications of intensity. It is probable, however, that spectrometric and spectrographic observations of powder reflections furnish the simplest way now open to obtain reliable scattering measurements.

Chapter VII. A Generally Applicable Method for Determining the Structures of Crystals

All of the ways of arranging the atoms of a crystal can be written down through the use of the theory of space groups (Chapter I). In Chapters IV, V and VI methods for producing and recording the diffraction effects which result when X-rays strike upon crystals have been described and in Chapter III equations are offered that express, as well as may be, the influence which the arrangement of the atoms within a crystal has upon the positions and intensities of these diffraction effects. With this information at hand a method can be outlined for deciding between the possible atomic groupings in crystals.

The essential steps of this method of crystal analysis are the following:

1. The determination of the amount of mass (the number of chemical molecules) associated with a crystallographically possible unit cell;

2. The determination of the correct unit cell for the atomic arrangement;

3. A statement of all of the possible atomic groupings which are compatible with this unit cell and with the symmetry requirements of the crystal;

4. A selection between these possible structures through the use of the attainable diffraction data.

Whenever all of these steps are carried through, either the correct atomic arrangement in a crystal is found or, if the experimental data are insufficient to attain this end, all structures which remain possibilities are known with certainty. If one or more of these steps are omitted or incompletely treated, as is often the case, then the resulting structure may agree with the limited experimental data that were used but there is no assurance that it is more than one of a number of otherwise unknown possibilities.

This chapter will be devoted to a consideration of certain details of each of the parts of a crystal analysis as outlined above. Many more or less complete examples of such analyses are outlined in the second part of this book.

1. **The Mass Associated with a Possible Unit Cell.**—Any unit cell not incompatible with the symmetry characteristics of a crystal is crystal-

lographically possible. For the initial determination of associated mass that unit may be used which has a shape defined by the customary axial ratios and angles. The nature of such unit cells for each of the systems of crystal symmetry has been outlined (page 60).

The volume (V) of a triclinic unit cell [1] is given by the expression:

$$V = a_0 b_0 c_0 \sin\beta \sin\gamma \sin\delta, \quad \text{where}$$

$$\sin\frac{\delta}{2} = \sqrt{\frac{\sin\left(\frac{\alpha-\beta+\gamma}{2}\right)\sin\left(\frac{\alpha+\beta-\gamma}{2}\right)}{\sin\beta\sin\gamma}} \quad \ldots \quad (27a)$$

For units having the symmetry of the other crystal systems this equation immediately reduces to:

Monoclinic unit:	$V = a_0 b_0 c_0 \sin\gamma$	(27b)
Orthorhombic unit	$V = a_0 b_0 c_0$	(27c)
Tetragonal unit:	$V = a_0^2 c_0$	(27d)
Cubic unit:	$V = a_0^3$	(27e)
Hexagonal unit:	$V = a_0^2 c_0 \sin 60°$	(27f)
Rhombohedral unit:	$V = a_0^3 \sin^2\alpha \sin\delta'$ where $\sin\frac{1}{2}\delta' = \sin\frac{1}{2}\alpha / \sin\alpha$	(27g)

This volume (V) is related to the mass within the unit and the density of the crystal through the simple density relation

$$\rho = mM/V \quad \ldots \quad (28)$$

where, as usual, ρ is the density of the crystal, M is the mass of its chemical molecule and m is the number of these molecules contained within the cell.

Substituting the volume of a unit cube (27e) in the preceding equation

$$\rho = mM / a_0^3 \text{ or } m = \rho a_0^3 / M$$

In this equation(ρ) is an easily measurable physical property of the crystal and M is the product of the molecular weight into the mass of a hypothetical atom of unit atomic weight (that is, approximately the mass of the atom of hydrogen). This latter quantity is given by the various estimates of the number of atoms within a gram atom of any element and has a value close to 1.65×10^{-24} grams. Though the length of the unit cell [for cubic crystals equal to the distance apart of geometrically alike (100) planes] cannot be found by any direct observation, X-ray reflections from a face (hkl) give d_{hkl}/n. Assuming then that a spacing measurement from a

[1] E. H. Kraus and G. Mez, Zeitsch. f. Kryst. *34*, 390 (1901).

cube face is available the ratio m/n^3 (the number of molecules in the unit divided by the cube of the order of reflection) is given by

$$m/n^3 = \rho\,(d_{100}/n)^3/M.$$

It often happens either that the crystal under investigation has such a habit that cube reflections cannot be readily obtained or that no crystals of any sort large enough for individual reflections can be grown. The spacing of any plane (hkl) is related to the length of the edge of the unit cube through the equation

$$d_{hkl} = a_0/(h^2 + k^2 + l^2)^{\frac{1}{2}} = d_{100}/(h^2 + k^2 + l^2)^{\frac{1}{2}} \quad \text{(15a) of Chapter III.}$$

If this value of d_{100} is introduced into the preceding formula the ratio of m/n^3 can be obtained from a spacing measurement upon any plane (hkl) through

$$m/n^3 = \frac{\rho}{M}\,(d_{hkl}/n)^3\,[h^2 + k^2 + l^2]^{\frac{3}{2}} \quad . \; . \; . \; . \; (29a)$$

In a similar way by substituting the appropriate forms of expressions (27) and (15) into equation (28), the following values of m/n^3 are found for unit cells belonging to the other systems of symmetry:

For the tetragonal unit:

$$m/n^3 = \frac{\rho c}{M}\,(d_{hkl}/n)^3\,[h^2 + k^2 + (l/c)^2]^{\frac{3}{2}} \quad . \; . \; . \; . \; (29b)$$

For the orthorhombic unit:

$$m/n^3 = \frac{ab\rho}{M}\,(d_{hkl}/n)^3\,[(h/a)^2 + (k/b)^2 + l^2]^{\frac{3}{2}} \quad . \; . \; . \; . \; (29c)$$

For the hexagonal unit:

$$m/n^3 = \frac{c\rho \sin 60^\circ}{M}\,(d_{hkl}/n)^3\,[4/3(h^2 + hk + k^2) + (l/c)^2]^{\frac{3}{2}} \quad . \; . \; . \; (29d)$$

For the rhombohedral unit:

$$m/n^3 = \frac{\rho \sin^2\alpha \sin\delta'\,(d_{hkl}/n)^3}{M[1 + 2\cos^3\alpha - 3\cos^2\alpha]^{\frac{3}{2}}}\,[(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + hl)(\cos^2\alpha - \cos\alpha)]^{\frac{3}{2}} \quad . \; . \; . \; (29e)$$

For the monoclinic unit:

$$m/n^3 = \frac{ab\rho \sin\gamma}{M}\,(d_{hkl}/n)^3\left[\frac{(h/a)^2 + (k/b)^2 - \frac{2hk}{ab}\cos\gamma}{\sin^2\gamma} + l^2\right]^{\frac{3}{2}} \quad (29f)$$

For the triclinic unit:

$$m/n^3 = \frac{ac\rho \sin\beta \sin\gamma \sin\delta}{M} (d_{hkl}/n)^3 \times$$

$$\left[\begin{vmatrix} h/a & \cos\gamma & \cos\beta \\ k & 1 & \cos\alpha \\ l/c & \cos\alpha & 1 \end{vmatrix} + k \begin{vmatrix} 1 & h/a & \cos\beta \\ \cos\gamma & k & \cos\alpha \\ \cos\beta & l/c & 1 \end{vmatrix} + l/c \begin{vmatrix} 1 & \cos\gamma & h/a \\ \cos\gamma & 1 & k \\ \cos\beta & \cos\alpha & l/c \end{vmatrix} \right]^{\frac{1}{2}} \Big/ \begin{vmatrix} 1 & \cos\gamma & \cos\beta \\ \cos\gamma & 1 & \cos\alpha \\ \cos\beta & \cos\alpha & 1 \end{vmatrix} \quad . \quad . \quad . \quad . \quad (29g)$$

Not only are both m and n integral but experiment seems to show that n is a small number. From this it follows that as long as the unit cell contains one or more atomic groupings ("molecules") all alike (so that no cells are encountered which contain for instance, five or seven chemical molecules), the ratio m/n^3 from any crystal will equal one of the numbers shown in the body of Table I. The use of this table can be illustrated by the following examples. The introduction of the spacings measured from (111) reflections of $K_2Zn(CN)_4$ crystals into expression (29a) gives $m/n^3 = 0.298$; reference to the table shows that the unit cube must contain either eight (n = 3) or 64 (n = 6) molecules. In the same way it is found that for calcite ($CaCO_3$) the spacing against the cleavage face ($d_{100}/n = 3.028A°$) yields the value $m/n^3 = 0.50$ for a unit with the shape of the cleavage rhombohedron ($\alpha = 101°55'$); consequently a unit of this shape will hold either four (n = 2) or 32 (n = 4) chemical molecules. If a crystal is a solid solution and not a single chemical compound it is then necessary to use an averaged molecular weight in the preceding calculations.

2. The Correct Unit Cell.—By the correct or "true" unit cell is to be understood the smallest prism which by simple repetition along the coördinate axes will build up the entire crystal. For cubic crystals there is no ambiguity in the choice of the correctly oriented unit for there is only one way of drawing cubic axes of reference. The only uncertainty that can then exist is whether the correct unit is the smallest one compatible with those reflections studied or whether it is necessary to increase the length of the edge of this small unit to some integral multiple. In actual practice that unit must be chosen as the correct one which, while agreeing with the experimental data, will still yield first order reflections from some atomic planes.

The difficulty experienced in establishing this correct unit cell for crystals of less than cubic symmetry constitutes perhaps the greatest immediate barrier to the extension of reliable crystal structure information. It is always possible, though it may prove tedious, to determine

TABLE I. VALUES OF m/n^3 FOR DIFFERENT VALUES OF m AND n

n \ m	1	2	3	4	6	8	12	16	24	32	48	64	96	192
1	1	2	3	4	6	8	12	—	—	—	—	—	—	—
2	0.125	0.250	0.375	0.500	0.750	1	1.500	2	3	4	6	8	12	—
3	.037	.074	.111	.148	.222	0.296	0.444	0.592	0.889	1.184	1.778	2.370	3.555	7.111
4	.016	.031	.047	.062	.094	.125	.187	.250	.375	.500	0.750	1	1.500	3
5	.008	.016	.024	.032	.048	.064	.096	.128	.192	.256	.384	.512	.768	1.536
6	.004	.009	.014	.018	.028	.037	.055	.074	.111	.148	.222	.296	.444	.888

the simplest unit which will agree with the available X-ray data; but in none of the studies yet made of crystals with less than cubic symmetry have all but one of the geometrically possible units been conclusively eliminated.

The most satisfactory data now attainable for choosing between possible unit cells are furnished by the Laue photographs. Not only will the values of $n\lambda$ calculated for all reflections be greater than the wave length minimum of the X-ray beam when the correct unit is chosen, but an intensity-wave length curve (Figure 110) drawn through the planes of a single form must meet the position of zero intensity at this λ_{min}. These requirements furnish the available criteria upon which the selection of correct unit cells must now be based. As a first step it is convenient to refer the Laue photographic reflections to a unit built upon the crystallographic axial ratios and angles and to calculate the corresponding values of $n\lambda$ with it and the appropriate form of equation (16). The requirements just outlined will not usually be fulfilled by the set of wave lengths thus obtained and the various other crystallographically possible unit cells with their different sets of planar indices must then be tested by computing their series of $n\lambda$. In theory the spectrometer measurements as well as Laue photographs should be useful in this search for the correct unit cell of non-cubic crystals. Frequently, however, changes in the unit cell do not alter the values of $n\lambda$ calculated from the simple planes ordinarily studied with the spectrometer.

This method of choosing between unit cells for a crystal will be illustrated by some data from a Laue photograph of rhodochrosite [1] ($MnCO_3$). The shape and dimensions of the unit rhombohedron corresponding to the dotted coördinate system of Figure 101, as determined by a knowledge of the symmetry properties and orientation of the crystal and by a reflec-

TABLE II. DATA FROM A LAUE PHOTOGRAPH OF $MnCO_3$

ACCORDING TO UNIT (A)		ACCORDING TO UNIT (B)	
Indices	$n\lambda$	Indices	$n\lambda$
$\bar{2}13$	0.408A°	$41\bar{1}$	0.408A°
$\bar{3}25$	.309	$72\bar{1}$	.309
$\bar{3}17$	.252	$42\bar{1}$	.504
$\bar{3}15$	.244	$31\bar{1}$	.488
$\bar{3}34$	.348	710	.348
$\bar{5}57$	.209	610	.418
$\bar{5}$, 11, 7	.211	913	.422
$3\bar{3}5$	.362	140	.724
$1,\bar{3}$, 11	.214	$46\bar{1}$	.428
$\bar{3}19$	.163	$43\bar{2}$	.326
$\bar{3}$, 1, 13	.193	$75\bar{1}$	.386
$0\bar{1}8$	.344	$78\bar{1}$	.344

[1] R. W. G. Wyckoff, Am. J. Sci. *50*, 317 (1920).

tion spectrum measurement from some face, are shown by the dotted rhombohedron (A) of Figure 144. The introduction of these dimensions and the indices of reflecting planes (from Figure 101) into equation (16e) will lead to data of which those of the first two columns of Table II are typical. The further knowledge of the voltage applied to the X-ray

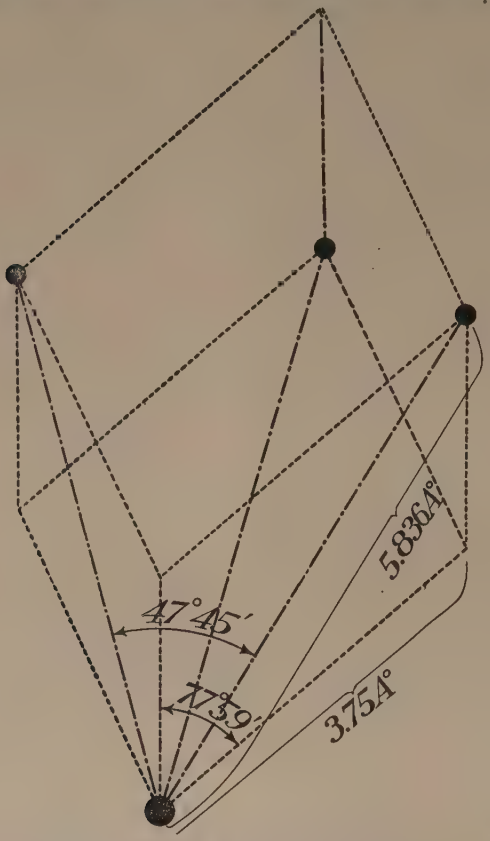


FIG. 144.—The size and shape of the rhombohedral unit cell corresponding to the dashed coördinate lines of Fig. 99 are shown by the dashed lines of this figure; the length and position of the edges of the unit cell which fits the diffraction data are shown by the dot-and-dash lines.

tube during the preparation of the Laue photograph shows (page 68) that the shortest X-rays present had the length $\lambda = 0.25A°$. Since calculations with the chosen unit cell give values of $n\lambda$ far below 0.25A°, it cannot be a possible one for rhodochrosite. The next simplest unit (B) has for its edges the diagonals of the first and is shown by the dot-and-dash lines of Figure 144. The indices of reflecting planes according to this new unit could be found by drawing the appropriate coördinate

system in Figure 101; they are, however, more simply calculated with the transformation equations

$$h' = k + l;\ k' = h + l;\ l' = h + k,$$

where (hkl) and (h'k'l') are the Miller indices of a plane according to the first and the new sets of axes respectively. The application of these new data in equation (16e) yields the values of $n\lambda$ given in the fourth column of Table II. Many reflections now lie in the first order region, none have values of $n\lambda$ less than 0.25A° and if a plot of $n\lambda$ against intensity (like Figure 110) were made for all observed reflections it would be found that the reflections stop quite sharply at 0.25A° and that intensities reach a decided maximum in the neighborhood of 0.46 − 0.48A°. In thus satisfying all attainable diffraction data this unit is a possible one for rhodochrosite. A similar treatment of the other less simple imaginable units would serve either to retain or eliminate them from further consideration in the search for the correct atomic arrangement.

From this illustration it is clear that Laue photographs furnish abundant data for deciding between geometrically possible unit cells. Inasmuch as an experimental selection between units is thus possible and because the results of experiment do not show that the crystallographically chosen axes always define unit cells, some sort of selection between units forms a necessary part of any reliable crystal structure determination. The results of a satisfactory investigation will state not only the units which agree with all attainable experimental data but also the nature of those geometrically conceivable units which were tried and found to be physically impossible.

3. **The Possible Atomic Arrangements.**—A use of the results of the theory of space groups is imperative at this point in the study of the structure of a crystal. All conceivable atomic arrangements can then be immediately written down from tables [1] giving all the possible atomic positions, if both the symmetry of the crystal and the number of molecules within the permissible unit cell, or cells, are known.

External Symmetry and the Symmetry of Atomic Arrangement. — This step in crystal analysis would be straightforward were it not that the relation is sometimes uncertain between the symmetry of the atomic arrangement in a crystal and what has customarily been taken as its symmetry of crystalline form (external symmetry). In the crystallographic assignment of symmetry not only are studies of optical properties brought to the aid of measurements of the nature and positions of the faces occurring upon a crystal but use has also been made of such less

[1] R. W. G. Wyckoff, An Analytical Expression of the Results of the Theory of Space Groups, Publ. 318, Carnegie Institution of Washington (1922).

understood phenomena as etch-figures and growth forms. X-ray diffraction measurements have definitely shown that the symmetry of atomic arrangement in a crystal does not always agree with the symmetry given it by etch-figures and studies of form development. Ammonium chloride furnishes the best example of this disagreement now available. Etch-figures and some observations upon rare faces [1] seemingly place this crystal in the enantimorphic hemihedral (plagihedral) class of the cubic system; diffraction effects aided by the results of the theory of space groups [2] show, on the other hand, that the symmetry of atomic arrangement is hemimorphic hemihedral (or holohedral, if the hydrogen atoms do not occupy positions which meet the requirements of symmetry). It becomes of great importance not only to search for the reason for such discrepancies as this but to discover which of the crystallographic indications of symmetry may be safely used as an aid in crystal analysis.

It has always been a basic assumption of descriptive crystallography that the "symmetry" of a crystal is the lowest that is defined by the symmetry of the distribution of its faces. With the possible exception of ammonium chloride there is yet no case of a conflict between the symmetry of face development and that of the atomic arrangement deduced with X-rays when all the faces of characteristic forms have been found developed upon crystals. There are nevertheless several instances (of which the alkali halides are typical) where a partial development of faces of a form has led to a supposed external symmetry less than or different from that of the atomic arrangement. Etch-figures have also been frequently employed in making assignments to a particular class of symmetry within a predetermined system. In their use it has been assumed that the shapes and distributions of these pits will conform to the "symmetry" of the entire crystal. The etch-figure symmetry of a crystal is often different for different conditions of etching and may be different from the symmetry arising from studies of face development. In all such cases it has been the working rule of crystallography to take as the "true" symmetry of a crystal the lowest that can be found by any procedure.

Though all 32 of the possible classes of crystal symmetry cannot be distinguished in this manner, a study of the optical properties of crystals gives evidence of their symmetry. Further indications are furnished by the phenomena of pyro- and piezo-electricity. In the symmetry of their X-ray diffraction effects all crystals divide themselves into eleven groups.

Of these various methods for determining crystal symmetry, etch-figures and face development (and solution bodies) — the symmetry

[1] See P. Groth, Chemische Krystallographie, Vol. I, 182 (1906).
[2] R. W. G. Wyckoff, Am. J. Sci. *3*, 177 (1922); *4*, 469 (1922).

criteria which have sometimes been found to be out of accord with results of crystal analysis — are surface phenomena. The atomic arrangement found in a crystal at considerable depths below its surface (its crystal structure) must be only one of several factors which influence its form and shape on growth and solution: the distribution of the forces about an atom lying on the surface of a crystal can scarcely be the same as it would be about a similar atom in the body of the crystal. From this standpoint it is not surprising to find the symmetry indicated by surface phenomena somewhat different from that of the atomic arrangement. If this point of view is correct then no conflict will ever be encountered between crystal structure data and optical or piezo-electric data (or X-ray diffraction effects); a low symmetry of atomic arrangement will be reflected in the observed face development, and other surface properties, but surface indications of a low symmetry need not correspond to a low symmetry of atomic grouping.

Ammonium chloride is the only crystal yet encountered which has a symmetry of atomic arrangement different from, and not simply higher than, the observed crystallographic symmetry; and a subsequent study of the crystal structures of the ammonium alums suggests that this may be only an apparent exception.[1] It has been found that in the alums there is no chemically permissible way of placing the hydrogen atom of the ammonium groups so that they will have positions which conform to the symmetry of the crystal as a whole (see page 363). As a consequence it is seen that in its symmetry properties, as well as chemically, the ammonium group in the alums behaves as a single entity which has essentially spherical symmetry. If the ammonium group can act as a sphere in the alums, it may also do so in all ammonium salts; in that case the symmetry of the atomic arrangement in ammonium chloride is holohedral instead of hemimorphic hemihedral. Future work will doubtless throw additional light upon this apparent violation of the fundamental assumption underlying all crystal structure investigation — that the positions of the atoms in a crystal conform to its symmetry. The violation is largely a formal one because an ammonium hydrogen atom presumably would be no longer possessed of electrons and consequently could give no appreciable indications of its position by its influence on either light or X-rays.

[1] If it is universally true that the symmetry deduced from surface phenomena may be lower than but not otherwise different from that of the atomic arrangement, it might be argued that these symmetry indications are correct and that low symmetry properties reside in the shapes of the atoms themselves. Against this point of view is the fact that no real evidence exists from other sources to suggest that the shape of the atom has any influence upon crystal symmetry; neither have there ever been found any of the gyroidal properties which should be possessed by such crystals as the alkali halides if they actually have less than holohedral symmetry of atomic arrangement.

If, as the preceding discussion suggests, the symmetry of atomic arrangement in crystals is the same as that found by optical methods but may be greater than that indicated by symmetry determinations based upon surface phenomena, in some cases of crystal structure examination it will be necessary to treat the possible arrangements that can be deduced from more than one class of symmetry. Though this increases the required labor, it can always be done.

Quite aside from the reasons arising from the conflicts in symmetry properties that have just been discussed, symmetry assignments made by any other method should be reinforced by an optical examination before they are used in crystal analysis. Frequently either a crystal of low symmetry has axial ratios and angles close to those of a crystal of higher symmetry or it approaches a more symmetrical form by twinning or other form of multiple growth. Thus potassium triiodide (KI_3) is pseudo-cubic in the first manner, ammonium iodate (NH_4IO_3) in the second. A crystal formed at one temperature sometimes inverts without change in external shape on passing to another temperature; the anisotropic character of crystals of leucite [$KAl(SiO_3)_2$], which externally appear cubic, is explained by the occurrence of such an inversion.

Once the symmetry, or possible symmetries, have been settled upon, all of the ways in which the atoms of a crystal can be arranged within its unit cell are immediately obtainable from the results of the theory of space groups. The previous determination of the number of molecules in the unit furnishes the number of atoms of each kind that must be placed in it. All of the chemically like atoms may be crystallographically alike or some may be related differently from others to the surrounding atoms. Both possibilities must be considered unless one or the other can be eliminated for sound reasons. A distinction between the various possibilities of arrangement may be made upon two grounds — (1) the symmetry requirements, (2) the necessity of having a structure which is chemically reasonable. Of these the first is entirely definite as far as it goes; but as long as the connections between crystal structure and chemical constitution remain as little understood as they are at present, great caution must be exercised in employing limitations of the second sort.

Possible Atomic Arrangements for Sodium Chloride. — The following treatment of the comparatively simple case of sodium chloride will serve to illustrate the way in which space group results are actually used in listing possible atomic arrangements. If only atomic groupings with holohedral symmetry (point group Oi) are considered, then a reference to the appropriate tables [1] shows that with four molecules of NaCl in

[1] R. W. G. Wyckoff, An Analytical Expression of the Results of the Theory of Space Groups, Publ. 318, Carnegie Institution of Washington.

the unit cube the following arrangements are the only conceivable ones. The four sodium atoms in the unit (1) might be similarly related to one another or it may be imagined (2) that three of them are alike but different from the fourth, (3) that two of them are different from the other two or (4) that all four are unlike.

(1) If the four sodium atoms are equivalent and the four chlorine atoms are also equivalent, the following atomic arrangements are seen to be possible:

(a) Na: 000; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$.
Cl: $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}00$; $0\frac{1}{2}0$; $00\frac{1}{2}$.
(b) Na: $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}\frac{3}{4}$; $\frac{3}{4}\frac{1}{4}\frac{3}{4}$; $\frac{3}{4}\frac{3}{4}\frac{1}{4}$.
Cl: $\frac{3}{4}\frac{3}{4}\frac{3}{4}$; $\frac{3}{4}\frac{1}{4}\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}\frac{1}{4}$; $\frac{1}{4}\frac{1}{4}\frac{3}{4}$.

By transferring its origin to the point $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ the second arrangement is, however, shown to be identical with the first.

(2) If three of the atoms of a chemical kind are equivalent but different from the fourth:

(c) Na: 000 and $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$.
Cl: $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and $00\frac{1}{2}$; $0\frac{1}{2}0$; $\frac{1}{2}00$.
(d) Na: 000 and $00\frac{1}{2}$; $0\frac{1}{2}0$; $\frac{1}{2}00$.
Cl: $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$.

In the positions of its atoms arrangement (c) is indistinguishable from (a) and (b).

(3) If the chemically like atoms fall into two groups of two geometrically equivalent atoms each: Since there is but one group of two equivalent positions possessing cubic symmetry, no arrangement of this sort is possible.

(4) If the four chemically like atoms are non-equivalent to one another: Since there are only two groups of singly equivalent positions in space groups with cubic symmetry, no such arrangement is possible.

In this way it may be concluded that if sodium chloride has holohedral symmetry and contains four molecules within its unit (a) and (d) are the only possible structures.

If merely for purposes of illustration it were admitted that NaCl can be assigned to any other class of cubic symmetry, the following structures with less than holohedral symmetry are found from a consideration of the space groups of these other point groups. They all belong to (1), in which the four chemically like atoms are also geometrically equivalent:

(e) From the space groups T–1 and Te–1:
Na: uuu; $\bar{u}u\bar{u}$; $\bar{u}\bar{u}u$; $u\bar{u}\bar{u}$.
Cl: a similar term in v.

(f) From the space group T–4:
Na: uuu; $u + \frac{1}{2}, \frac{1}{2} - u, \bar{u}$; $\bar{u}, u + \frac{1}{2}, \frac{1}{2} - u$; $\frac{1}{2} - u, \bar{u}, u + \frac{1}{2}$.
Cl: a similar term in v.

(g) From the space group Te–2:
Na: 000; $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$.
Cl: $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}\frac{3}{4}$; $\frac{3}{4}\frac{1}{4}\frac{3}{4}$; $\frac{3}{4}\frac{3}{4}\frac{1}{4}$

Indistinguishable from (g) are other arrangements obtained by taking the remaining combinations of the four sets of equivalent positions of (a) and (b) two at a time.

(h) From the space group O–6:
Na: $\frac{1}{8}\frac{1}{8}\frac{1}{8}$; $\frac{3}{8}\frac{3}{8}\frac{7}{8}$; $\frac{7}{8}\frac{5}{8}\frac{3}{8}$; $\frac{3}{8}\frac{7}{8}\frac{5}{8}$.
Cl: $\frac{5}{8}\frac{5}{8}\frac{5}{8}$; $\frac{1}{8}\frac{7}{8}\frac{3}{8}$; $\frac{3}{8}\frac{1}{8}\frac{7}{8}$; $\frac{7}{8}\frac{3}{8}\frac{1}{8}$.

(i) From the space group O–7:
Na: $\frac{3}{8}\frac{3}{8}\frac{3}{8}$; $\frac{7}{8}\frac{1}{8}\frac{5}{8}$; $\frac{5}{8}\frac{7}{8}\frac{1}{8}$; $\frac{1}{8}\frac{5}{8}\frac{7}{8}$.
Cl: $\frac{5}{8}\frac{1}{8}\frac{3}{8}$; $\frac{1}{8}\frac{3}{8}\frac{5}{8}$; $\frac{3}{8}\frac{5}{8}\frac{1}{8}$; $\frac{7}{8}\frac{7}{8}\frac{7}{8}$.

The conceivable atomic arrangements for any other crystal can be written down in this same way by inspecting the tabulations of the space groups having its determined symmetry. For crystals with cubic symmetry the possible structures will usually be comparatively few in number but with crystals of lower symmetry they may become very numerous. The many arrangements which must then be tested one by one with X-ray diffraction data are an important factor operating to prevent more adequate studies of crystals of low symmetry.

If a crystal is of such chemical complexity that it contains atoms with appreciable scattering powers in generally equivalent positions (page 64), the space group of the correct structure can often be determined in advance of a knowledge of its atomic arrangement. Where this can be done the number of possible groupings that require individual treatment will be greatly lessened. This selection between space groups, which follows along similar lines to those used in choosing between the various individual structures, will be discussed with them in the following section. Space group criteria based upon Laue photographic [1] and spectrum photographic data, have been presented for cubic crystals; similar distinctions can also be drawn among crystals with lower symmetry.[2]

4. **The Choice of the Correct Structure.**—After the possible atomic arrangements have been written down, the diffraction effects to be expected from each of them can be qualitatively calculated using expression (20). Having found out in this way the characteristic differences in their diffrac-

[1] R. W. G. Wyckoff, Am. J. Sci. *4*, 175 (1922).
[2] P. Niggli, Geometrische Krystallographie des Discontinuums, Kapitel IV (Leipzig, 1919).

tion effects, the correct structure can be sought with whichever diffraction experiments will give the most valuable results.

If the structure is simple, like that of sodium chloride, all of the atoms occupy positions which are completely determined by symmetry requirements. In these groupings with fixed parameters the structure consequently is entirely known as soon as the correct arrangement has been found. Some atoms in most crystals, however, are defined by one or more coördinates with values not established by the dictates of symmetry. The preceding arrangements (e) and (f) for sodium chloride are such structures. In these cases it is necessary to determine by reference to the appropriate diffraction data first the correct arrangement and then, if possible, to evaluate the variable parameters. If there is only one variable in the structure it can be obtained with considerable accuracy and complete assurance of correctness. The large amount of labor involved in getting results which are at best only approximate makes it rarely if ever worthwhile to try to place the atoms in structures with more than two independent variables. When the interrelations between the structure and the chemical properties of crystals are more thoroughly understood and when the scattering powers of atoms are better evaluated, the variable ranges requiring examination will be much narrowed and more such parameters can then be successfully treated.

A Selection between Structures for Sodium Chloride. — The general procedure to be followed in testing out the structures possible for a crystal can be illustrated by the following treatment of arrangements (a), (d) and (g) for sodium chloride. It consists essentially in calculating with expression (20) of Chapter III the diffraction effects characteristic of each of these arrangements and comparing them with the necessary diffraction observations.

For arrangement (a): $I \propto A^2 + B^2$. There results by substituting the coördinates of atomic positions into expression (20):

$$A = \overline{Na}[\cos 2\pi n(0) + \cos \pi n(k + l) + \cos \pi n(h + l) + \cos \pi n(h + k) + \overline{Cl}[\cos \pi n(h + k + l) + \cos \pi nh + \cos \pi nk + \cos \pi nl]; \quad B = 0$$

This reduces to:

(1) When n is odd:

If h, k and l are all odd, $A = \overline{Na}[4] - \overline{Cl}[4]$

If h, k and l are two even and one odd, $A = \overline{Na}[0] + \overline{Cl}[0]$

If h, k and l are two odd and one even, $A = \overline{Na}[0] + \overline{Cl}[0]$

(2) When n is even, $A = \overline{Na}[4] + \overline{Cl}[4]$ always.

Thus it is seen that with this arrangement of atoms there will be strong even order reflections from all planes. Odd order reflections, of an ampli-

tude which represents the opposition in phase of waves from the two kinds of atoms, will be observed only from planes with all odd indices. The atomic numbers, and scattering powers, of sodium and chlorine atoms are not very different and these odd order reflections will be weak; if, as is approximately true for potassium chloride, the two kinds of atoms in this arrangement had identical scattering powers, no reflections of any sort would be found in the odd orders.

For arrangement (d):

$$A = \overline{Na}[1 + \cos \pi nh + \cos \pi nk + \cos \pi nl] + \overline{Cl}[\cos \pi n(h + k + l) + \cos \pi n(h + k) + \cos \pi n(h + l) + \cos \pi n(k + l)]; \; B = 0.$$

This reduces to:

(1) When n is odd

If h, k and l are all odd, $A = \overline{Na}[-2] + \overline{Cl}[2]$
If h, k and l are two even and one odd, $A = \overline{Na}[2] - \overline{Cl}[2]$
If h, k and l are two odd and one even, $A = \overline{Na}[0] + \overline{Cl}[0]$.

(2) When n is even, $A = \overline{Na}[4] + \overline{Cl}[4]$ always.

This arrangement likewise will give second order reflections from all planes, but both all odd and two even and one odd reflections will appear, rather faintly, in odd orders.

For arrangement (g):

$$A = \overline{Na}[1 + \cos \pi n(h + k) + \cos \pi n(k + l) + \cos \pi n(h + l)] + \overline{Cl}[\cos \tfrac{\pi}{2} n(h + k + l) + \cos \tfrac{\pi}{2} n(h + 3k + 3l) + \cos \tfrac{\pi}{2} n(3h + k + 3l) + \cos \tfrac{\pi}{2} n(3h + 3k + l)];$$

$$B = \overline{Na}[0] + \overline{Cl}[\sin \tfrac{\pi}{2} n(h + k + l) + \sin \tfrac{\pi}{2} n(h + 3k + 3l) + \sin \tfrac{\pi}{2} n(3h + k + 3l) + \sin \tfrac{\pi}{2} n(3h + 3k + l)].$$

This reduces to:

(1) When n is odd

If h, k and l are all odd, $A = \overline{Na}[4] + \overline{Cl}[0]$; $B = \overline{Na}[0] + \overline{Cl}[\pm 4]$ and therefore $I \propto (4\overline{Na})^2 + (4\overline{Cl})^2$.
If h, k and l are two even and one odd, $A = \overline{Na}[0] + \overline{Cl}[0]$; $B = \overline{Na}[0] + \overline{Cl}[0]$.
If h, k and l are two odd and one even, $A = \overline{Na}[0] + \overline{Cl}[0]$; $B = \overline{Na}[0] + \overline{Cl}[0]$.

(2) When n is even, $A = \overline{Na}[4] + \overline{Cl}[4]$; $B = 0$ always. The diffrac-

tion effects from this structure resemble those from (a) but with the important difference that since the waves from the two kinds of atoms are now adding together, the odd order reflections from planes with all odd indices will have a considerable intensity.

A study of the diffraction effects produced by sodium chloride shows strong second order reflections from all sorts of planes and only weak first order reflections from planes with all odd indices (page 304). As a result (d) may be immediately excluded from further consideration. A better choice between (a) and (g) can be made by calculating the approximate relative intensities of first and second order reflections from planes with all odd indices. By writing the atomic numbers (or better the electron numbers of the ions) for $\overline{\mathrm{Na}}$ and $\overline{\mathrm{Cl}}$ and substituting the amplitudes just discussed in expression (26), it is readily shown that (a) but not (g) is in good accord with the intensities of powder reflections.

The Determination of a Variable Parameter. — If a structure contains one variable parameter it is best determined by calculating the expected amplitudes (or intensities) for different values of the parameter. The calculated intensities can be compared with experiment after being plotted. For instance in sodium nitrate (see page 346) [1] the amplitude of first order reflections having either all odd or two even and one odd indices is proportional to

$$B = 2\overline{O}[\sin 2\pi u(h - k) + \sin 2\pi u(l - h) + \sin 2\pi u(k - l)].$$

All such planes with the following values for $(h - k)$, $(l - h)$ and $(k - l)$ are present in Laue photographs: $\bar{1}, \bar{2}, 3$; $\bar{1}, \bar{1}, 2$; $2, 3, \bar{5}$; $7, \bar{2}, \bar{5}$. The curves of Figure 145, which were prepared by substituting these differences in the preceding expression agree in all having a considerable amplitude near the point $u = 0.25$. A more accurate placing of the oxygen atoms could probably be obtained by the use of other curves for different observed reflections; if enough data are available it is frequently possible to locate the atomic position very accurately. In practice it is often of advantage to use comparisons of relative intensities for this purpose, but in doing this the decline of intensity with spacing must be taken into account. Reliable results can then be expected only when comparisons are made between planes with the same spacings or when complicated planes (with smaller spacings) are found to be at least as intense as simpler ones. If sufficient data are obtainable and the necessary care is exercised in their interpretation atoms can be satisfactorily located in this way; but if errors are to be avoided it is essential that the "laws" of scattering underlying these approximate intensity calculations be not taken too literally. This process of determining atomic

[1] R. W. G. Wyckoff, Phys. Rev. *16*, 149 (1920).

positions is applied to the study of structures with one or more variables in many of the investigations subsequently to be reviewed (Part II).

The Determination of the Space Group of a Cubic Crystal. — The characteristic diffraction effects that would be produced by atoms lying in the general positions of every space group can be calculated by the same procedure which has been illustrated for sodium chloride. The results

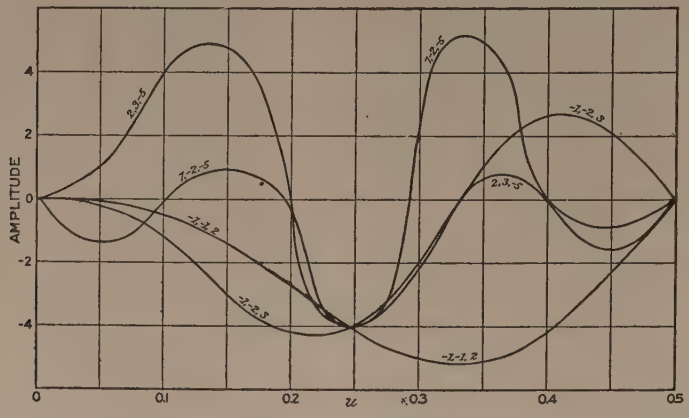


FIG. 145.—Curves obtained by plotting calculated amplitudes of reflection against values of u for several first order reflections from $NaNO_3$. The numbers attached to these curves are the corresponding values of h–k, l–h and k–l.

of such calculations for the cubic groups [1] are stated in Table III; qualitative distinctions can be made between most of these groups. The type of atomic arrangement can consequently be obtained with great ease for crystals having atoms of appreciable scattering power in the generally equivalent positions of one of these uniquely determined space groups. It will be noted that for such determinations there is no need of a knowledge of the corresponding class of symmetry; rather, the symmetry (of atomic arrangement) is itself deduced with entire certainty from the diffraction measurements alone. The diffraction effects from some of these cubic groups, however, differ only in the presence or absence of reflections of planes of a single form, [100]. It frequently happens that the positions and the relative scattering powers of the atoms of a crystal may be such that reflections from these planes, though present, will be weak. It is therefore safe to use the presence but not the absence of a single planar reflection for distinguishing between space groups; for this same reason reflections from several forms must be examined before any of the criteria based upon the absence of reflections can be considered to be fulfilled.

[1] R. W. G. Wyckoff, Am. J. Sci. *4*, 175 (1922).

The application of these space group criteria will be illustrated by a determination of the atomic arrangement in cubic crystals of $Zn(BrO_3)_2 . 6H_2O$. The symmetry of their Laue photographs is that of the point groups T and Ti rather than Te, O and Oi. An analysis of the Laue photographic data in the usual fashion showed the presence of first order reflections having all kinds of indices. The fundamental lattice must therefore be the simple cubic lattice. A distinction (Table III) between the space

TABLE III. THE CHARACTERISTIC DIFFRACTION EFFECTS OF THE CUBIC SPACE GROUPS

A. Space Groups based upon a *Simple Cubic Lattice*, in general all three kinds of planes appearing in all orders:

1. Hemihedral Photographs:

T−1 and Ti−1: No classes of planes absent;
T−4: Planes of the form [100] absent in odd orders;
Ti−2: Planes of the form [0kl], where k and l are one even and the other odd, are absent in odd orders;
Ti−6: Planes of the form [h0l], where h is even and l is odd, and of the form [0kl], where k and l are both odd, are absent in the odd orders.

2. Holohedral Photographs:

Te−1, O−1 and Oi−1: No classes of planes absent;
Te−4 and Oi−3: Planes of the form [hkl], where h = ± k and either h is even and l is odd or both h and l are odd, are absent in odd orders;
O−2: Planes of the form [100] are absent in odd orders;
O−6 and O−7: Planes of the form [100] are absent in all but the fourth, eighth, etc. orders;
Oi−2: Planes of the form [0kl], where k is even and l is odd, and of the form [hhl], where either h is even and l odd or both h and l are odd, are absent in odd orders;
Oi−4: Planes of the form [0kl], where k is even and l is odd, are absent in the odd orders.

B. Space Groups based upon a *Face Centered Cubic Lattice*, in general planes having all odd indices appearing in odd orders:

1. Hemihedral Photographs:

T−2, Ti−3 and Ti−4: No classes of all odd planes are absent in the first order. Second order reflections are absent from Ti−4 for planes of the forms [0hl] and [h0l], where h is even and l is odd.

2. Holohedral Photographs:

Te−2, O−3, O−4, Oi−5 and Oi−7: No classes of all odd planes are absent in odd orders. From O−4 only fourth, eighth, etc. orders from planes of the form [100] are present. Second order reflections from Oi—7 are absent for planes of the form [0kl] where k is even and l is odd;
Te−5, Oi−6 and Oi−8: Planes with all odd indices are present in odd orders except those of the form [hkl], where h = ±k. Second order reflections from Oi − 8 of planes of the form [0kl], where k is even and l odd, are absent.

C. Space Groups based upon a *Body Centered Cubic Lattice*, in general planes having two odd and one even indices appearing in odd orders:

1. Hemihedral Photographs:

   T−3, T−5 and Ti−5: No classes of two odd and one even planes are absent;
   Ti−7: Planes of the form [0kl], where k and l are both odd, are absent from odd orders.

2. Holohedral Photographs:

   Te−3, O−5, O−8 and Oi−9: No classes of two odd and one even planes are absent in the first order. Reflections in the second order from planes of the form [100] are absent for O−8;
   Te−6: Planes of the form [hll], where $\frac{1}{2}$ h is even and l odd, are absent in odd orders. In the second order planes of the forms [hhl], where either h is even and l odd or both h and l are odd, are absent;
   Oi−10: Planes of the form [0kl], where k and l are odd, and of the form [hll], where $\frac{1}{2}$ h is even and l is odd, are absent in the first order. Reflections in the second order are absent for planes of the forms [hhl], where either h is even and l odd or both h and l are odd.

groups built upon this lattice and giving hemihedral Laue photographs is to be made through a study of reflections from planes of the forms [0kl] and [h0l]. Examination of the Laue data reveals the fact that though numerous reflections from planes of the forms [0kl], where k is odd and l is even, are to be found in the first order region, no reflections can be detected from planes of the forms [0lk] or of the forms [0kh], where h also is odd. It is thus certain from Table III that the space group of $Zn(BrO_3)_2 \cdot 6H_2O$ must be Ti–6. Once this has been established an inspection of the possible atomic positions under this space group,[1] combined with the knowledge that four molecules are contained within the unit cube (as deduced from a reflection spectrum measurement and from Laue data), tells immediately that the only admissible arrangement of the atoms in this crystal is the following:

Zinc atoms: 4b, 000; $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$.

Bromine atoms: 8h, uuu; $u + \frac{1}{2}, \frac{1}{2} - u, \bar{u}$; etc.
$\bar{u}\bar{u}\bar{u}$; $\frac{1}{2} - u, u + \frac{1}{2}, u$; etc.

Bromate oxygen atoms: the 24 generally equivalent positions xyz; etc.

Hydrate oxygen atoms: the 24 generally equivalent positions xyz; etc., with different values of the parameters x, y and z.

Though this method of establishing the space group of a crystal is most useful, and, in fact, makes the determination of atomic arrange-

[1] R. W. G. Wyckoff, An Analytical Expression of the Results of the Theory of Space Groups (Washington, 1922), p. 127.

ment easier for a complicated than for a simple cubic crystal, care must be taken in its application. Dependable results will be obtained from its full use only if the atoms in generally equivalent positions have appreciable scattering powers and do not approach too close to arrangements with other symmetry properties. Crystals of $Ni(NO_3)_2.6NH_3$ illustrate these dangers. Laue data obtained from them are in entire agreement with a structure having the symmetry of the space group Oi–5; but a chemically plausible arrangement cannot be found and calculation shows that a suitable structure based upon Ti–6 will not give diffraction effects which deviate by a detectable amount from the seemingly holohedral ones that are observed.

Similar criteria will doubtless prove useful in the investigation of other than cubic crystals and in selecting between arrangements composed of atoms in special instead of general positions. Even in their present form the cubic criteria can often be successfully used to eliminate structures without atoms in general positions. The calculation and classification of the diffraction effects from all possible atomic arrangements is an arduous task which will require a long time for its completion. Such knowledge, however, when it does become available will make possible much more powerful and more carefully ordered methods of analysis.

Chapter VIII. A Brief Historical Outline of the Development of Existing X-ray Diffraction Methods

It is impossible to give a perfectly fair historical account of the growth of methods of diffraction analysis — too large a part of progress in any field of science has its origin not only in the daily environment but in the chance contacts and discussions of those persons making it. For this reason, if for no other, little more will be attempted here than a chronological statement of the process by which existing methods have become available.

The idea that X-rays can be diffracted arose from the interaction between the very old theoretical view of a crystal as a regular and indefinitely extended arrangement of atoms or molecules and the prevailing hypotheses concerning the nature of the X-rays themselves. For many years after their discovery, the fundamental character of X-rays was completely in doubt. By many they were supposed to be a corpuscular form of radiation (like the electrons, for example). Others thought that they were the irregular "ether" pulses called forth by electrons striking the target of an X-ray tube. Some considered them to be wave motions — longitudinal with great wave length, mixed longitudinal and transverse, transverse with very long wave lengths and transverse with very short wave lengths. In order to discriminate between these hypotheses various unsuccessful attempts were made to refract and to reflect X-rays. Further efforts to diffract X-rays through small apertures showed that if they were transverse wave motions analogous to ordinary light, as much of the existing evidence seemed to indicate, their wave lengths must be not appreciably greater than 10^{-9} cm. The knowledge of the number of atoms in the gram molecule of a substance had already shown that the mean distance apart of the neighboring atoms in a crystal is of the order of 10^{-8} cm. With this information at hand and at a time when active attempts were being made to explain various optical properties of a crystal from the standpoint of structure theory,[1] M. Laue [2] suggested that if X-rays are such short waves, the regular arrangement of atoms which constitutes

[1] P. P. Ewald, Inaug. Dissertation, München, 1912.
[1] M. Laue, W. Friedrich and P. Knipping, Sitzungsber. Bayer. Akad. Wiss. (Math.-phys. Klasse) 1912, p. 303; Ann. d. Phys. *41*, 971 (1913).

a crystal ought to act towards them as a kind of three-dimensional diffraction grating. These ideas proved to be correct, for when the experiment of passing a pin-hole beam of X-rays through a thin section of copper sulfate crystal was tried,[1] the now familiar spot photograph (Chapter IV) was obtained. When subsequent observations had shown that the type of diffraction pattern thus prepared was dependent upon the crystal used and conformed to its symmetry requirements, a way became conceivable for the investigation of the internal constitution of crystalline solids.

The subsequent development of orderly methods of structure determination from this fundamental experiment has arisen through the use of information of both a theoretical and an experimental character. Ever since it became customary to look upon a crystal as an assemblage of atoms a chief concern of theoretical crystallographers has been the definition of all the atomic groupings which could have the symmetry of crystals. This problem appears to have found its final answer in the completion of the theory of space groups a little less than a decade before the discovery of X-rays.

The origins of this theory lie in the beginnings of crystallographic thought.[2] It commenced to assume definite and precise form, however, with the work of Frankenheim and Bravais upon space lattices. The lattices define merely the patterns according to which atomic groupings are repeated throughout space. They all possess the complete symmetry of the system to which they belong and it was necessary to search for an explanation of tetartohedral and hemihedral properties in the arrangement of the atoms within these atomic groups. After the growth of the mathematical theory of groups had made it possible, such an extension of the symmetry requirements to atomic positions was made by Sohncke. In this way he succeeded in defining all of the space groupings of symmetry elements which would give rise to "molecules" having the same shape and a like orientation throughout a crystal. The theory of space groups thus begun was completed by the introduction of the concept of an enantiomorphic arrangement of the atomic groupings through the almost simultaneous efforts of E. Fedorov, A. Schoenflies and W. Barlow. To make them directly useful in determining the structures of crystals it has, however, been necessary not only to give the results of space group theory an analytical expression but to extend them to all possible atomic positions through the deduction of the special cases (Chapter I).

[1] M. Laue, W. Friedrich and P. Knipping, Sitzungsber. Bayer. Akad. Wiss. (Math.-phys. Klasse) 1912, p. 303; Ann. d. Phys. *41*, 971 (1913).

[2] More or less detailed reviews of the development of the theory of space groups are given by L. Sohncke, Entwickelung einer Theorie der Krystallstruktur (Leipzig, 1879); Barlow, Miers and Smith, Report Brit. Assoc. p. 297 (1901); R. W. G. Wyckoff, The Analytical Expression of the Results of the Theory of Space Groups (Washington, 1922).

The resulting ability to write down all possible atomic arrangements for a crystal would be of no practical importance if it were not at the same time possible to distinguish between them. It is the ability of X-ray diffraction effects to make these distinctions to a greater or less extent which has brought the subject of crystal structure study out of the realm of pure speculation into the field of experimentally determinable science.

Together with the observation showing the existence of the X-ray diffractions Laue presented a theory [1] to account for them as arising from the interference of trains of X-ray waves scattered by the atoms of the diffracting crystal. Zinc blende (ZnS) was treated in this way upon the assumption that it was built up of molecules arranged upon a simple cubic lattice and that the X-ray beam consisted of rays of five different wave lengths. W. L. Bragg [2] showed that the data are more consistent with the hypothesis that the diffraction spots arose from the scattering of a beam of "white" X-rays by molecules having a face-centered grouping (in accordance with the demands of the now discredited valency-volume hypothesis of Barlow and Pope); he further proposed that the phenomena are more easily described as reflections from parallel planes of atoms within the crystal. This explanation implied that X-rays should be "reflected" from the faces of crystals and led to the development of the X-ray spectrometer.[3] Around this instrument has grown up the entire field of X-ray spectroscopy. At the same time the various crystal structures suggested with its aid have focused attention upon the usefulness of diffraction methods in experimental investigations of crystal structure.

An X-ray analysis of zinc blende and the accurate placing of the sulfur atoms in pyrite [4] emphasized the larger amount of information that can now be obtained from Laue photographs. The essence of these studies underlies most subsequent work with Laue photographs.

From the experimental standpoint the third outstanding development has been the extension of diffraction methods to crystalline powders. It is natural that after diffraction effects had been produced with single crystals, attempts should be made to get them from all manner of substances. They were sought from powders, liquids, fibers and substances in various other special states of aggregation. Though a sort of band was thus observed from a crystalline powder [5] the use of heterochromatic X-rays made it impossible to obtain a clearly defined pattern. When later a tube

[1] M. Laue; W. Friedrich and P. Knipping, Sitzungsber. Bayer. Akad. Wiss.(Math.-Phys. Klasse) 1912, p. 303; Ann. d. Phys. *41*, 971 (1913).
[2] W. L. Bragg, Proc. Camb. Phil. Soc. *17*, I, 43 (1912).
[3] W. H. and W. L. Bragg, Proc. Roy. Soc. A. *88*, 428 (1913).
[4] P. P. Ewald, Ann. d. Physik *44*, 257 (1914); P. P. Ewald and W. Friedrich, ibid. *44*, 1183 (1914).
[5] W. Friedrich, Physikal. Z. *14*, 317 (1913).

operated to emit nearly monochromatic X-rays was employed, usable powder photographs became realities.[1]

A science of crystal structure determination began to arise when a meeting was effected between these experimental methods of diffraction study and the results of theoretical crystallography. At least two independent and only slightly related efforts to develop adequate methods of study have been made. One of these has arisen through contributions from several continental European workers (Ewald, Gross, Niggli, Schiebold, Aminoff, etc.); the other, the essentials of which have been outlined in the preceding chapters and will be illustrated in Part II of this book, had its origins in early attempts of S. Nishikawa[2] to use space group results in studies of crystal structure.

[1] P. Debye and P. Scherrer, Physikal. Z. *17*, 277 (1916); A. W. Hull, Phys. Rev. *10*, 661 (1917).

[2] S. Nishikawa, Proc. Math. Phys. Soc. Tokyo *8*, 199 (1915).

PART II

THE RESULTS OF CRYSTAL ANALYSIS

Chapter IX. An Introduction to the Discussion of Existing Crystal Structure Results

In the preceding chapters the available methods for determining atomic positions in crystals have been reviewed and a procedure has been outlined which in its essence is applicable to the investigation of all crystals. Largely because of the problems involved in a choice of the true unit cell the satisfactory assurance of correctness achieved through a treatment of all possible atomic arrangements has been obtained only for cubic crystals. The simplest arrangements which are in agreement with the attainable diffraction data have been deduced for a few crystals of hexagonal and tetragonal symmetry; their degree of probable correctness is very large in some cases but it has not been exactly evaluated. Inasmuch as an experimental selection between geometrically possible unit cells can now be made, little weight can, or will, be attached to the results of crystal structure studies which do not choose between these units using all significant attainable data.

If it were true that the geometrically simplest arrangements or those which seemed simplest in the light of the existing chemical and other preconceptions are the correct atomic arrangements in crystals, then a great emphasis on the necessity of treating experimentally all possible atomic arrangements would perhaps be of only formal interest. The reliable data show, however, that such is not in fact the case. Thus simple crystal structures which seem chemically and crystallographically plausible can readily be imagined for pyrrhotite of the composition FeS or for carborundum (CSi); nevertheless the actual atomic arrangements in both appear to be much more complicated. The worthlessness of apparent chemical analogies and relationships as a means of predicting crystal structures finds many illustrations. For instance silver and cuprous oxides have the same structure but the cuprous halides have one atomic arrangement (the zinc sulfide grouping), silver chloride and bromide have another one (the sodium chloride grouping) which is in turn different from the stable modification of silver iodide (the zinc oxide arrangement); similarly all of the cesium halides have an ammonium chloride-like structure except the fluoride which resembles the other alkali halides in being structurally isomorphous with sodium chloride. This present failure of prediction as applied to the results of crystal analysis is the

greatest encouragement to pursue its development; for if its results could be foretold experimental studies with X-rays would have little, while in reality they must eventually have much, to contribute towards the problems of the laws governing atomic combination.

At the same time the impossibility of prediction must mean that only those crystal structures can be treated as authentic and reliable for which the determinations of atomic arrangement have been made unique. Such unique structures, in the search for which every possible atomic grouping will have been considered in detail, can only be achieved through the use of the results of the theory of space groups in some such general procedure as has been outlined in PART I. For this reason there is no alternative in the subsequent discussion of the existing crystal structure data but to apply to them and to their results the criteria of correctness and uniqueness which this point of view implies. An effort has been made to treat all of the useful crystal structure data from this one standpoint. In the case of cubic crystals the steps required for the deduction of the correct atomic arrangement are outlined for each crystal; in the deduction of possibly correct structures for other crystals an attempt has been made to state clearly the limiting assumptions that have been used. In this way it is sought to make the existing crystal structure information as nearly homogeneous a whole as is now possible. It is a consequence of this mode of treatment that the data of various investigators have been approached from a standpoint not their own and that the responsibility rests with the present writer in all cases for the form, and in many instances for the substance of the arguments based upon these measurements.

The available data prove that unaided powder observations may lead to erroneous determinations of structure for even simple crystals; thus agreement in position to the extent of 20 lines has been found with a simple cubic structure for lithium iodide (LiI) from a material which was not anhydrous lithium iodide and can scarcely have been cubic in symmetry. Other examples of the same sort are frequently encountered. The existing information likewise shows that spectrometric observations as ordinarily carried out may lead to totally incorrect atomic arrangements through the recording of extraneous reflections: the alums and some data from sodium chlorate (*1921*, 37) supply such instances. It is consequently necessary to exclude from detailed consideration all those diffraction studies which consist solely of spectrometer observations made in the usual way.

In discussing the diffraction data from crystals it is necessary to have some order in presentation. It is preferable that this order be one sufficiently elastic and comprehensive to include future investigations as well.

Such a scheme of classification is already available in the ones used for crystallographic description. Of these the two most widely used are probably those of Dana (System of Mineralogy) and of Groth (Chemische Kristallographie). Both are, perhaps of necessity, more or less arbitrary in their groupings of related crystals. Although that of Groth is in many respects the less natural, it has for the present purposes the great advantage of including organic crystals; hence its major outlines will be followed.

The next four chapters will be devoted to a consideration of diffraction data which have been used for crystal structure determinations and to the description of the atomic arrangements which can be legitimately deduced from these data. One of the two concluding chapters (XIV) will be given over to a description of the various kinds of diffraction effects which have been observed from matter in other than the crystalline state of aggregation; Chapter XV discusses briefly some of the uses to which diffraction data and the resulting crystal structure knowledge have been put. Many of these applications to the older branches of science (for instance the study of alloys and of minerals) are just beginning; others, such as the bearing of crystal structure data upon the existence of "cubical" (or other "stationary" electron) atoms are undoubtedly of only passing interest.

The literature references of PART II are contained in the bibliography which forms Supplement I. The titles of this bibliography have been arranged by years and are referred to throughout the text of the subsequent chapters by making, for example (*1913*, 1) relate to the first paper listed (in this collection) for the year 1913.

Chapter X. The Crystal Structures of Elements and of Metallic Alloys

The Diffraction Data Upon Elements of Group I

The Alkali Metals.—Powder photographic, but no other, data have been obtained from lithium, sodium and potassium. Metallic potassium yields only a general blackening at ordinary temperature (*1917*, 9) but crystalline diffraction is definite at $-150°$ C, although the individual crystals were too large to give a good powder photograph. This failure of potassium at room temperature to furnish a crystalline diffraction pattern has been interpreted to mean that it is amorphous. Well defined crystals of potassium have, however, been grown from the molten metal and potassium has a definite and sharp latent heat of fusion and melting point. Its giving only amorphous scattering is then probably to be attributed rather to the large amplitudes of thermal agitation of its atoms than to any lack of order in their arrangement. Cooling of such a material should result in the successive appearance and gradual strengthening of a crystalline pattern at the expense of the general blackening. This experiment has not yet been tried upon potassium. Sodium, however, with a higher melting point shows such a poor crystalline pattern upon a much blackened background.[1]

The data from two studies of lithium, though meager, are in substantial agreement with one another. An examination of another specimen gave additional lines which were not identified (*1917*, 9) but probably are to be ascribed to a hydration or other alteration product.[2] If it is assumed that these metals have cubic symmetry, the positions of the powder lines from lithium and sodium combined with their densities show agreement with the reflections from planes with simple indices when $m/n^3 = 2$. Reference (*1922*, 111) to space group tabulations shows that the only cubic arrangement possible for two like atoms is the simple body centered one [2a] with the coördinates:

$$000;\ \tfrac{1}{2}\tfrac{1}{2}\tfrac{1} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \qquad [2a]$$

[1] The observed failure of sodium prepared from molten metal to give any diffraction lines may have been due not to its lack of crystallinity but to the presence of only a very few crystals in the specimen.

[2] The ease with which these extraneous lines could be given the indices of a cubic crystal is an interesting illustration of the dangers of unaided powder spectroscopy.

The approximate intensities of powder reflections from such an atomic grouping can be found by use of expression (26), of Chapter VI, to possess the following characteristics:

$$I \propto (d/n)^{2.35} [\overline{N}\,(1 + \cos\pi n\,\{h + k + l\})]^2 \times j \quad . \quad . \quad . \quad . \quad (30),$$

When n is odd:

$I = 0$ if h, k and l are either two even and one odd or all odd,
$I \propto (d/n)^{2.35}\,[2\overline{N}]^2$ if h, k and l are two odd and one even.

When n is even:

$I \propto (d/n)^{2.35}\,[2N]^2$ always.

It will be seen from this expression that no matter what may be the atomic number N of the scattering atom the relative intensities, which alone can now be measured, of reflections from all crystals with this atomic arrangement will be the same (assuming, of course, that the atoms can always be treated as dimensionless scattering centers).

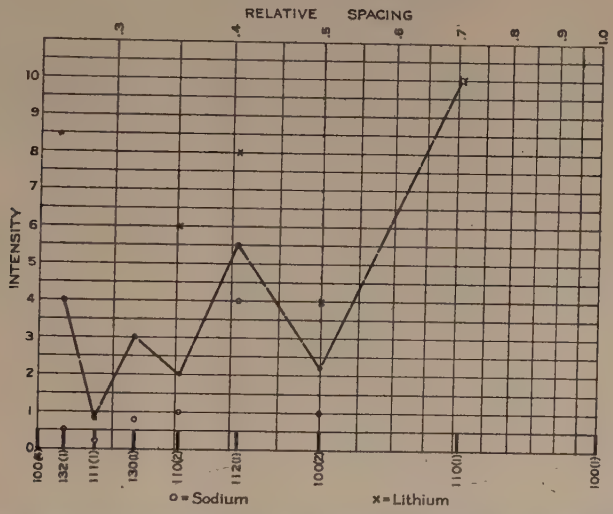


FIG. 146.—The relative intensities of the principal powder reflections from a "body centered" cubic arrangement of atoms [2a], as calculated from expression (30), are connected by the dashed lines of this figure. The observed relative intensities of powder lines of metallic lithium and sodium are shown by the crosses and open circles.

The relative intensities of the most important reflections calculated with expression (30) and reduced to a scale showing the intensity of the strongest observed line as ten are connected by the straight lines of Figure 146. The intensities of published powder data on sodium are shown upon the same scale as open circles; the lithium data (crosses) were prepared

for comparison by writing the following numbers for the published letter intensities: zs = 10, s = 8, ms = 6, m = 4.

The published intensity data upon powder photographs, even those expressed according to a numerical scale, are for the most part mere visual estimations. Not only for this reason but because expression (30), in its use of the "normal decline" cannot be strictly accurate, it is difficult to know how close an agreement to expect between calculation and observation. The fact that careful intensity estimates upon both light and heavy atoms (see, for instance, the data upon beryllium and iridium) fall closely upon their calculated values, when taken in connection with the accumulated experience on well-established structures, seems definitely to require that for *planes with large spacings* (the ones most commonly considered in powder photographs) the sequence of observed intensities will not deviate from those calculated. This is in reality a sensitive criterion for, while visual estimations of absolute intensity cannot be of more than the roughest sort, it is easily possible to detect slight differences in the relative intensities of two lines.

The agreement of intensities for both lithium and sodium with the simple structure [2a] are probably as good as the assumptions and the character of the observations require. It may consequently be concluded that if their crystals are cubic and have simple structures (the few data obtainable indicate both to be true) then the arrangement of their atoms must be the "body centered" one shown in Figure 147.

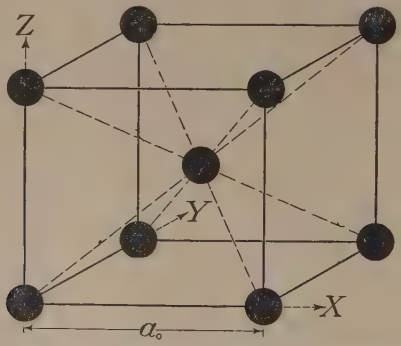


FIG. 147.—The unit cell of the "body centered" cubic arrangement of atoms, [2a].

Lithium. (*1917*, 9; *1921*, 13). The length of the edge of the unit cube containing two atoms is found to be 3.50A°. One set of these data (*1921*, 13) has been made the basis of an extended discussion of possible electronic arrangements in lithium atoms (*1923*, 13).

Sodium (*1917*, 9). The length of the edge of the unit cube containing two atoms is said to be 4.30A°.

Potassium (*1922*, 58). No data have been published upon this crystal, but it is said that the observations at − 150° C agree best with a body centered structure (Figure 147) for which $a_0 = 5.20A°$.

The Sub-group Elements. — Spectrometer measurements have been made on all three metals—copper, silver and gold. Powder reflections have been recorded from metallic gold and it has been reported (without any data) that similar observations upon the other two metals are in accord with their spectrometer data. Crystallographic measurements of face development on crystals of all three metals indicate cubic symmetry. The diffraction observations agree with this symmetry and together with the known density yield a value of $m/n^3 = 4$. No data are found to show that m is greater than four. The following are the only possible cubic arrangements of four chemically like atoms within a unit (*1922*, 111):

[4a] uuu; $u\bar{u}\bar{u}$; $\bar{u}u\bar{u}$; $\bar{u}\bar{u}u$.
[4b] 000; $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$.
[4f] uuu; $u + \frac{1}{2}$, $\frac{1}{2} - u$, $\bar{u}$; $\bar{u}$, $u + \frac{1}{2}$, $\frac{1}{2} - u$; $\frac{1}{2} - u$, $\bar{u}$, $u + \frac{1}{2}$.
[4g] 000; $\frac{1}{2}\frac{1}{4}\frac{3}{4}$; $\frac{3}{4}\frac{1}{2}\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}\frac{1}{2}$.
[4h] 000; $\frac{1}{2}\frac{3}{4}\frac{1}{4}$; $\frac{1}{4}\frac{1}{2}\frac{3}{4}$; $\frac{3}{4}\frac{1}{4}\frac{1}{2}$.

For all three metals odd order reflections are absent from planes with two odd and one even or two even and one odd indices. Consequently the failure to find first order reflections from (110), for instance, eliminates [4g] and [4h]; a similar use of the appropriate form of expression (20) shows that (contrary to the results of experiment) odd order reflections having other than all odd indices will appear from [4a] or [4f] unless u has values which make these arrangements approach [4b]. If the structures of these metals are simple ones containing four atoms within the unit (as the data indicate), their atomic arrangement must then be either [4b] or an indistinguishably close approach to it.

The phase factor, $(A^2 + B^2)$, of expression (20) will have the following form for [4b]:

When n is odd: . . . . . (31)

$A = 0$ if h, k and l are either two even and one odd or two odd and one even,
$A = (4\overline{N})$ if h, k and l are all odd;

When n is even:

$A = (4\overline{N})$ always.

The B term in all cases equals zero.
Thus from [4b] there will be present only all odd reflections in the odd orders and all sorts of reflections in the even orders. The sequence of

reflections in a powder photograph to which this arrangement would give rise is shown graphically by the points connected by straight lines in Figure 151 [assuming expression (26)]. It is obvious from the form of (31) that these relative intensities will be the same for all crystals having this atomic arrangement.

Copper. The reflections obtained from the (100), (110) and (111) faces of a single crystal (*1914*, 10) agree with the requirements of this "face centered" cubic arrangement [4b] (Figure 148). From these data the

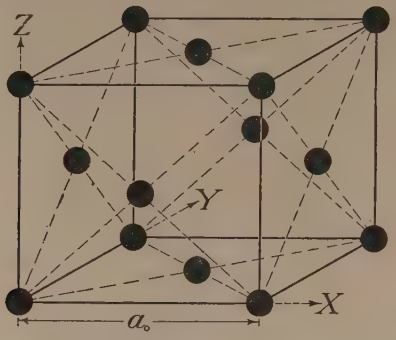


FIG. 148.—The unit cell of the "face centered" cubic arrangement of atoms, [4b].

length of the edge of the unit cube is $a_0 = 3.60A°$. A powder spectrometer measurement from a sheet of copper is said to give $a_0 = 3.628A°$ (*1923*, 72). Besides reports of powder measurements unaccompanied by data, a study of the solid solutions of copper and gold (*1922*, 52) has shown that the powder pattern of copper is analogous to that of gold. From this last study a_0 for copper is found to be 3.615A°.

Silver. Spectrometer measurements (*1916*, 30) similar to those made upon copper have been carried out upon natural crystals of silver. They show that the only possible simple structure is either [4b] (Figure 148) or a very close approach to it; from them the value of a_0 is 4.06A°. Powder measurements incidental to studies of the alloys of silver with palladium and silver with gold (*1922*, 63) have given (no detailed data on silver) $a_0 = 4.08A°$. Sputtered silver films are crystalline (*1921*, 60) and yield the usual powder pattern. The information upon evaporated films is contradictory, one observer finding a crystalline pattern (*1923*, 84), the other (*1921*, 60) seeing none. Colloidal suspensions of silver have been found to be crystalline with the same atomic arrangement that prevails in the macrocrystalline metal (*1920*, 52).

Gold. A single reflection (*1916*, 31) from an octahedral face gives $a_0 = 4.07A°$. Powder data from alloys with silver (*1922*, 63) are said to yield $a_0 = 4.075A°$ (no data recorded upon gold). The powder reflections

listed in Table I give $a_0 = 4.07$A° (*1920*, 52). The calculated intensities of these lines were obtained with expression (31); a comparison between them and the estimated intensities shows excellent agreement with the

Table I. Intensities of Powder Reflections from Gold

Indices	Intensity	
	Observed	Calc. for [4b]
111(1)	strong	10
100(2)	medium strong	5.4
110(2)	medium	4.7
113(1)	strong	6.5
111(2)	medium weak	1.9
100(4)	medium weak	1.0
133(1)	medium	3.3
120(2)	medium	3.2
112(2)	medium strong *	2.6
115(1) } 111(3) }	strong *	3.1

requirements of arrangement [4b] (Figure 148) except for the last two reflections (marked with an asterisk). These reflections took place through such large angles ($2\theta > 90°$) that they should be more intense than the calculations based upon (26) would suggest. Sputtered films of gold (*1921*, 60) furnish the same powder pattern as precipitated metal. Diffraction measurements have also been used to determine the particle size in samples of colloidal gold (see page 375).

The Elements of Group II

Powder photographs have been prepared from the two transitional elements—beryllium and magnesium—from the alkaline earth metal calcium and from zinc, cadmium and mercury.

The Transition Elements.—Crystallographic study indicates that magnesium is hexagonal with an axial ratio of $a : c = 1 : 1.624$. Its powder photographs agree with this symmetry and axial ratio. Photographs from beryllium also fit with an hexagonal structure for which $a : c = 1 : 1.580$. Besides the powder measurements individual crystals of magnesium have yielded a few spectrum photographs. These data in themselves are not sufficient to permit a satisfactory determination of atomic arrangement. Iridosmium, a natural alloy of iridium and osmium, seems to be crystallographically isomorphous with magnesium (for iridosmium $a : c = 1 : 1.590$). If it is *assumed* that the two metallic crystals have the same type of atomic arrangement, then a combination of the available Laue data from iridosmium (*1921*, 4) with the powder measurements upon magnesium permits the following treatment:

The Laue photographs appear to arise from untwinned specimens; if such is the case their complete hexagonal symmetry means that the crystals belong to one of the point groups 6d, 6e, 6D or 6Di. These Laue data are thought not to conflict (the agreement could be improved) with a unit cell having the customary orientation and axial ratio. Taking a similar unit for magnesium and beryllium, the following arrangements are possible (*1922*, 111) for the two atoms contained in such a cell:

[a] 000; 00u (or, 00u; 00ū).
[b] 000; $00\frac{1}{2}$.
[c] 000; $\frac{1}{3}\,\frac{2}{3}\,0$ (or, $\frac{1}{3}\,\frac{2}{3}$u; $\frac{2}{3}\,\frac{1}{3}$u).
[d] 000; $\frac{1}{3}\,\frac{2}{3}\,\frac{1}{2}$ (from, $\frac{1}{3}\,\frac{2}{3}\,\frac{1}{4}$; $\frac{2}{3}\,\frac{1}{3}\,\frac{3}{4}$).

Arrangement [a] arises from the space groups 6d − 1, 6d − 3, 6D − 1, 6Di − 1; the others come from these and other space groups isomorphous with 6d, 6e, 6D and 6Di. Grouping [b] is obviously only a special case of [a].

The intensity expressions (according to (26)) for powder reflections from these arrangements will have the following forms:

$$\text{(a')}\quad I \propto (d/n)^{2.35} \times j \times [\overline{N}^2 (1 + \cos 2\pi n\, l)^2 + \overline{N}^2 (\sin 2\pi n\, l)^2]$$

$$\text{(c')}\quad I \propto (d/n)^{2.35} \times j \times [\overline{N}^2 (1 + \cos 2\pi n \{\tfrac{1}{3}h + \tfrac{2}{3}k\})^2 + \overline{N}^2 (\sin 2\pi n \{\tfrac{1}{3}h + \tfrac{2}{3}k\})^2]$$

$$\text{(d')}\quad I \propto (d/n)^{2.35} \times j \times \overline{N}^2 [(1 + \cos 2\pi n \{\tfrac{1}{3}h + \tfrac{2}{3}k + \tfrac{1}{2}l\})^2 + (\sin 2\pi n \{\tfrac{1}{3}h + \tfrac{2}{3}k + \tfrac{1}{2}l\})^2] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

The estimated intensities of all the observed powder lines of beryllium (*1922*, 59) and magnesium (*1917*, 6, 9) down to 21·0(1) are shown in Figure 149. Expression (a') indicates that for the same order n all planes with the same l index will have the same phase factor; though 10·1(1) is the strongest line in the powder photographs, such simple reflections as 00·1(1) and 11·1(1) are entirely absent. As a consequence [a] and [b] are immediately eliminated. The failure of these same planes to reflect also shows grouping [c] to be impossible. It remains therefore to see how closely the existing diffraction data accord with [d]. One of the properties of [d] is the absence of odd order reflections from 00·1 and from hh·l if l is odd; these requirements are fulfilled by the data from beryllium, magnesium and iridosmium. The calculated intensities of the strongest reflections to appear from the first two, if the arrangement is [d], are connected by the dotted lines of Figure 149. As is true of the other structures for metals these relative intensities may be expected to be the same for all crystals having this atomic grouping. The agreement between experiment and calculation is excellent for beryllium.[1] Except for the apparent

[1] The reflection from 10·3(1) should not, however, be appreciably less than that of 11·0(1).

absence of a 00·1(2) reflection the data for magnesium are satisfactory. Such a 00·1(2) reflection was observed in the spectrum photographs (*1917*, 9). If its faintness is real one of two conclusions seems necessary.

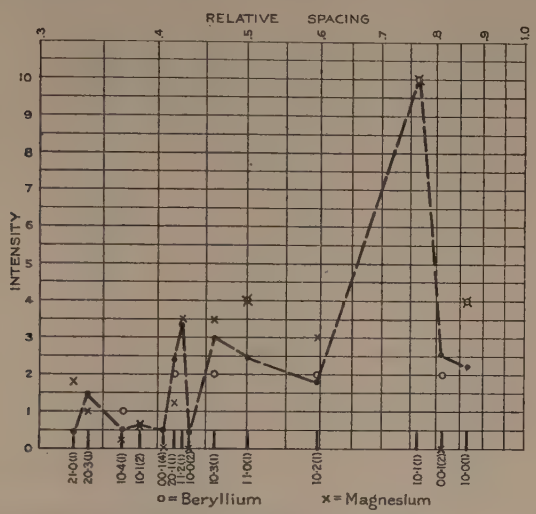


FIG. 149.—The calculated relative intensities of the principal powder reflections from the hexagonal close packed arrangement, [d], with axial ratio a : c = 1 : ± 1.60, are connected by the dashed lines of this figure. The observed relative intensities of powder lines of magnesium and beryllium are shown by the crosses and open circles.

Either the atoms in metallic magnesium have a definite orientation with respect to the crystal structure and their atomic structures are such as to depress the intensity of this reflection (an alternative which, though it cannot be conclusively disproved, is made improbable by the mass of existing diffraction data) or else one or more of the assumptions used in deducing the structure of magnesium crystals are not justified and the correct atomic arrangement is not the one which has been discussed. Thus it might be that magnesium has only three-fold symmetry so that the z-parameter of arrangement [d] can assume some other value than one half; or the correct atomic arrangement may be built upon some other of the crystallographically possible unit cells. For these reasons additional powder observations upon magnesium are needed.

In the light of the preceding discussion the available knowledge of the structures of beryllium and magnesium can be summarized as follows:

Beryllium (1922, 59).—The powder data are in satisfactory agreement with arrangement [d] (Figure 150). The dimensions of the unit cell thus containing two atoms are determined to be: a_0 (the base) = 2.283A°; c_0 (the height) = 3.607A°, corresponding to the usual axial ratio a : c = 1 : 1.580.

Magnesium.—Except for an unaccountable weakness of the 00·1(2) reflection, the powder data and some reflection spectra from individual crystal faces agree with arrangement [d] (Figure 150). According to different determinations the unit cell of this structure has the dimensions:

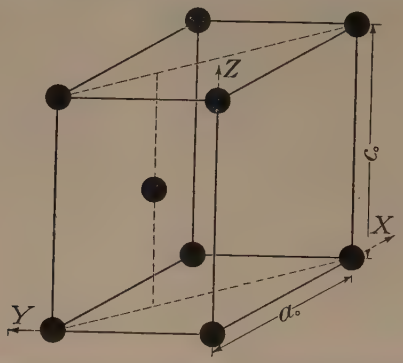


FIG. 150.—The unit cell of the hexagonal closest packed arrangements, [d].

$a_0 = 3.22A°$, $c_0 = 5.23A°$ (*1917*, 6, 9); $a_0 = 3.23A°$, $c_0 = 5.25A°$ (*1920*, 3); $a_0 = 3.17A°$, $c_0 = 5.17A°$ (*1923*, 72).

The Alkaline Earth Metals.—*Calcium* (*1920, 33*; *1921, 54*). On the basis of very fragmentary crystallographic observations metallic calcium has been supposed to possess hexagonal symmetry; its powder diffraction

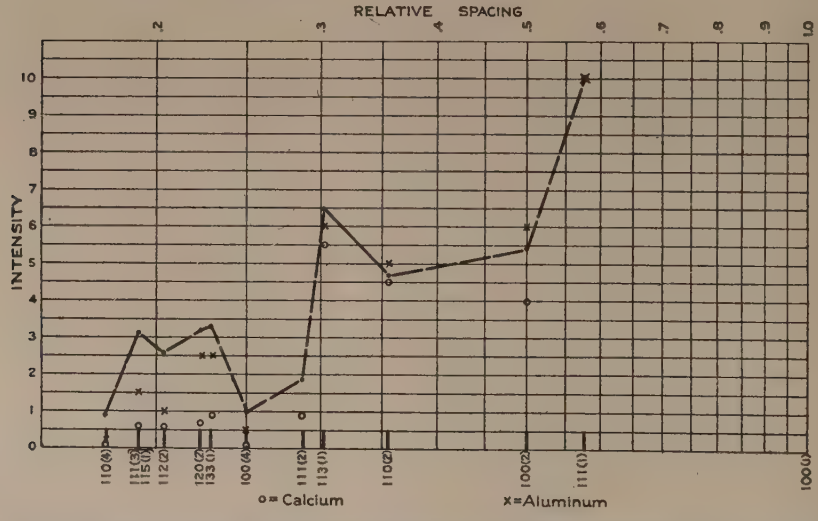


FIG. 151.—The calculated relative intensities of the principal powder lines from the "face centered" cubic arrangement, [4b], are connected by the dashed lines of this figure. The observed relative intensities of the chief powder reflections from aluminum and calcium are shown by crosses and open circles.

lines, however, agree in position with those of a cubic structure containing four atoms within the unit cell. In these powder experiments a comparison photograph of calcium oxide was used to eliminate effects due to direct oxidation of the metal powder. As Figure 151 shows the powder data are in excellent agreement with the face centered arrangement [4b] that has been discussed for copper, silver and gold. A repetition of the considerations of their previous treatment then will show that this structure (or an indistinguishably close approach to it) is the only possible one if, as the data seem to show, calcium is cubic and has a simple atomic arrangement. The length of the edge of such a unit cube (Figure 148) has been determined to be $a_0 = 5.56A°$.

The Sub-group Elements.—The powder photographs from the first two of these metals—zinc and cadmium—have the same general characteristics as those from magnesium and beryllium; it has consequently been supposed that they have the same hexagonal arrangement [d]. For zinc the axial ratio corresponding to this structure must be $a : c = 1 : 1.860$ rather than the crystallographically measured $a : c = 1 : 1.356$. This observation indicates that the inversion which takes place as zinc is cooled from its melting point does not destroy the crystal outlines of the high temperature form. Presumably for the same reason the axial ratio deduced from powder photographs of cadmium is different from that arising from a study of its external form. The two independent studies of crystalline mercury only agree in making it hexagonal with a structure different from the closest packing [d] supposed to prevail for the other hexagonal metals.

Zinc (*1921, 55*).—The extent of the agreement between the observed intensities of reflection and those calculated for the arrangement

$$000;\ \tfrac{1}{3}\tfrac{2}{3}\tfrac{1}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [d]$$

is shown in Figure 152. Though these intensities are satisfactory for planes with the largest and with small spacings, the reflections 10·3(1), 11·0(1), 11·2(1) and perhaps 20·1(1) cannot be so intense as these estimates indicate if the correct structure is exactly [d]. For this reason a reexamination of powder reflections is imperative before [d] can be finally accepted as probably correct. Measurements upon the powder photographs show that the unit cell containing two atoms will have the dimensions: $a_0 = 2.670A°$, $c_0 = 4.966A°$. An extensive study has been made of the phenomena accompanying the stretching of wires of zinc (*1922*, 57).

Cadmium (*1921, 55*).—The positions of the powder lines of cadmium conform to the demands of an arrangement [d] (Figure 150) which has the axial ratio $a : c = 1 : 1.89$ instead of the crystallographically determined $a : c = 1 : 1.335$. The extent of the agreement between observed intensities and those calculated for this closest packed structure is shown in

Figure 152. Except for too rapid a decline of intensity with spacing, which perhaps is due to absorption in the diffracting sample, the powder data fit very satisfactorily with the requirements of this simple structure

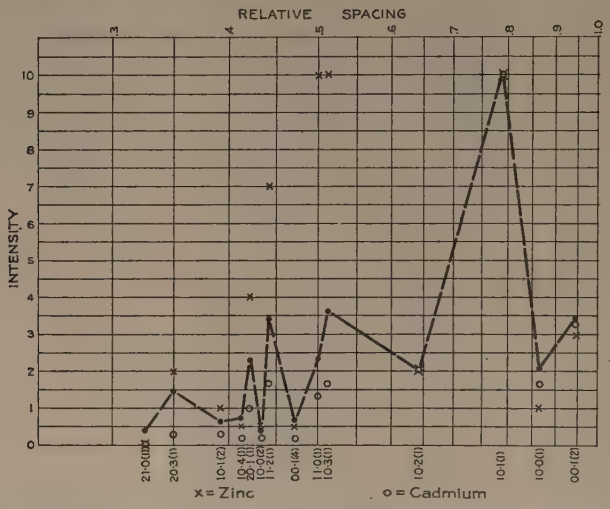


FIG. 152.—A plot comparing the observed relative intensities of the principal powder lines of zinc and cadmium with those calculated for an hexagonal close packed arrangement, [d], having the axial ratio $a : c = 1 : \pm 1.89$.

(Figure 150). The dimensions of its unit cell, as deduced from these data, are: $a_0 = 2.980$A°, $c_0 = 5.632$A°.

Mercury.—Two independent powder investigations have been made upon solid mercury. In one of them (*1922*, 1) the entire spectrograph was imbedded in solid carbon dioxide; for the other photographs (*1922*, 65) the specimen was maintained at the temperature of about −115° C. As the data of Table II make clear, there is utter disagreement between the experimental results of these two studies. Only future work can tell whether this is due to the existence of an inversion somewhere between

TABLE II. MERCURY POWDER REFLECTIONS WITH GREATEST SPACINGS AS FOUND BY

ALSEN AND AMINOFF		MCKEEHAN AND CIOFFI	
	HEXAGONAL		RHOMBOHEDRAL
SPACINGS	INDICES	SPACINGS	INDICES
3.62A°	00·1(2)	2.771A°	100(1)
3.37	10·0(1)	2.255	111(1)
3.02	10·1(1)	1.750	$10\bar{1}(1)$
2.46	10·2(1)	1.474	$11\bar{1}(1)$
1.95	10·3(1)	1.379	210(1)
1.92	11·0(1)	1.235	221(1)
1.805	00·1(4)		
1.705	11·2(1)		

the temperatures of these two investigations. One set of data (*1922*, 65) has been supposed to agree with a simple rhombohedral arrangement of atoms; the other (*1922*, 1) has been interpreted in terms of an hexagonal structure containing four atoms in the unit cell. The photographs from both experiments are said to be poor; no intensity measurements are furnished by which the second study may be judged. More work is obviously needed before reliable conclusions can be drawn concerning the structure of solid mercury.

The Elements of Group III

Powder data are available from aluminum and indium; though no further analysis was attempted, it has been shown that the strongest reflections of gallium are not those to be expected from a cubic crystal.[1]

Aluminum.—The positions of the observed powder reflections conform to the requirements of a cubic crystal containing four atoms in the unit. As Figure 151 shows the intensities (*1917*, 9) of these lines fit well with those calculated for arrangement [4b] (Figure 148). The length of the edge of such a unit cell has been variously found to be 4.05A° (*1917*, 8, 9), 4.07A° (*1918*, 25) and 4.040 ± 0.005A° (*1922*, 52).

Indium (*1921, 55*).—A powder photograph of indium has been interpreted to indicate that its atoms have a face centered arrangement in a tetragonal prism with the axial ratio a : c = 1 : 1.06. The data do not, however, seem sufficient to assure the probable correctness of this structure.

The Elements of Group IV

The Transition Elements.—X-ray diffraction patterns have been produced from many specimens of carbon. Except for those from the diamond only the diffraction lines characteristic of graphite were found in these experiments. In many kinds of "amorphous" carbon, however, the individual crystals are so extremely minute that their reflections are much widened. Both crystalline silicon and the so-called "amorphous" product have invariably been found to give the diamond type of pattern.

Carbon as Diamond (*1913, 6; 1917, 9*).—Enough data are at hand to establish with great certainty the atomic arrangement in the diamond. Both crystallographic and optical examinations leave no doubt of its cubic character. Reflections from an octahedral face combined with the density show that $m/n^3 = 8$. The data from the early Laue photographs, which are confirmed by powder measurements, give no reasons for taking a unit containing more than eight atoms.

[1] This statement is the result of measurements by the writer which have not yet been described in detail.

There are several ways (*1922*, 111) of arranging eight atoms so that they will have cubic symmetry. In order to abbreviate the treatment at this point it will be considered that these atoms are crystallographically as well as chemically alike; the other possibilities arising from an assumption of non-equivalence of all eight atoms can be eliminated by the same procedure which will now be applied to the case of eight like atoms. Of those structures having no variable parameters [8e] and [8i], (*1922*, 111), are alike; they are merely twice-scale reproductions of an arrangement [1a] built of atoms at the corners of the unit cell. Since first order reflections from an eight atom unit are observed, this grouping must be eliminated. Similarly the enantiomorphic arrangements [8l] and [8m] are excluded by the presence of first order reflections from planes with all odd indices. The only remaining structure ([8g] is the same grouping),

$$[8f] \quad 000;\ 0\tfrac{1}{2}\tfrac{1}{2};\ \tfrac{1}{2}0\tfrac{1}{2};\ \tfrac{1}{2}\tfrac{1}{2}0;\ \tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4};\ \tfrac{1}{4}\tfrac{3}{4}\tfrac{3}{4};\ \tfrac{3}{4}\tfrac{1}{4}\tfrac{3}{4};\ \tfrac{3}{4}\tfrac{3}{4}\tfrac{1}{4},$$

gives the following values to A and B of expression (20):

$$A = \bar{N}[1 + \cos \pi n(h + k) + \cos \pi n(h + l) + \cos \pi n(k + l) + \cos \tfrac{1}{2} \pi n(h + k + l) + \cos \tfrac{1}{2} \pi n(h + 3\ k + 3\ l) + \cos \tfrac{1}{2} \pi n(3h + k + 3\ l) + \cos \tfrac{1}{2} \pi n(3\ h + 3\ k + l)].$$

$$B = \bar{N}[\sin \tfrac{1}{2} \pi n(h + k + l) + \sin \tfrac{1}{2} \pi n(h + 3\ k + 3\ l) + \sin \tfrac{1}{2} \pi n(3\ h + k + 3\ l) + \sin \tfrac{1}{2} \pi n(3\ h + 3\ k + l)]; \quad . \ . \ . \ . \ . \ . \ . \ . \ (33)$$

When n is odd:

$A = 4\bar{N}$; $B = 4\bar{N}$, if the indices are all odd,
$A = B = 0$, if the indices are two even and one odd or two odd and one even.

When n is even:

If the indices are all odd or two even and one odd,
$A = B = 0$ when $n = 2, 6$, etc.
$A = 8\bar{N}$, $B = 0$ when $n = 4, 8$, etc.

If the indices are two odd and one even,
$A = 8\bar{N}$, $B = 0$ for all even values of n.

From these expressions (33), it follows that atoms in the positions of [8f] will give odd order reflections only from planes with all odd indices; second, sixth, etc., orders will appear only from planes with two odd and one even indices; fourth, eighth, etc., orders are found for all planes. The reflections observed in Laue photographs and with the spectrometer (*1913*, 6) agree with these requirements; powder photographs (*1917*, 9) give more effectively the same results. It could be shown that the several

arrangements with variable parameters cannot exactly meet these requirements unless u has a value which converts them into [8f] or [8g]. It therefore seems legitimate to conclude that the atomic arrangement in the diamond is either exactly [8f] (Figure 153) or an indistinguishably close approach to it.

A comparison between the observed and the calculated intensities of powder reflections from the diamond (*1917*, 9) is of great interest not

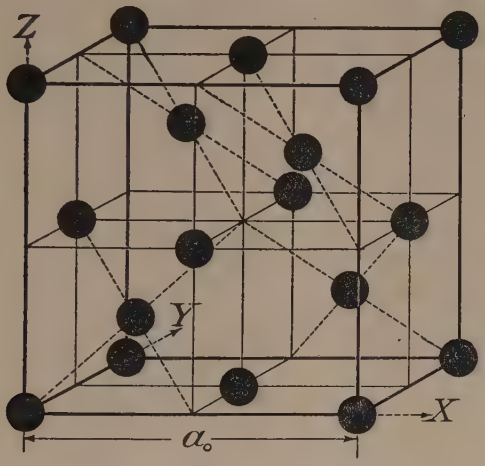


FIG. 153.—The unit cube of the diamond arrangement, [8f].

merely because of the few electrons in the carbon atom but because four of its six electrons should be shared by neighboring atoms if interatomic electron bonds actually exist. Except for too weak a 110(2) reflection, the intensities calculated according to (26) for [8f] are in surprisingly good agreement with observation (Figure 154). The apparent absence of any 111(2) reflections has been supposed (*1918*, 11; *1920*, 37) to indicate that electrons are not held in common by atoms in the diamond; in the face of our present inability to evaluate the effects of thermal agitation upon such weakly bound electrons, this conclusion is scarcely a necessary one. More recently it has been said that spectrometer observations (*1921*, 18) show evidence for the existence of such a reflection; if actually present it will be the only direct evidence from crystal analysis for the existence of bonding electrons and it will constitute the only known case of diffraction effects having *positions* which are not completely determined by the *atomic* arrangement. The importance of this result and the possibility of error inherent in the usual spectrometer technique suggest that additional spectrographic observations should be carried out.

The two determinations of the length of the edge of the unit cube containing eight atoms are: $a_0 = 3.55A°$ (*1913*, 6) and $3.56A°$ (*1917*, 9).

Carbon as Graphite.—No thoroughly satisfactory crystallographic determination of the symmetry of graphite has ever been possible. The best indications, together with a Laue photograph (*1914*, 17), and all of the existing powder data agree with its assignment to the hexagonal system. On the basis of powder measurements alone, two different atomic arrange-

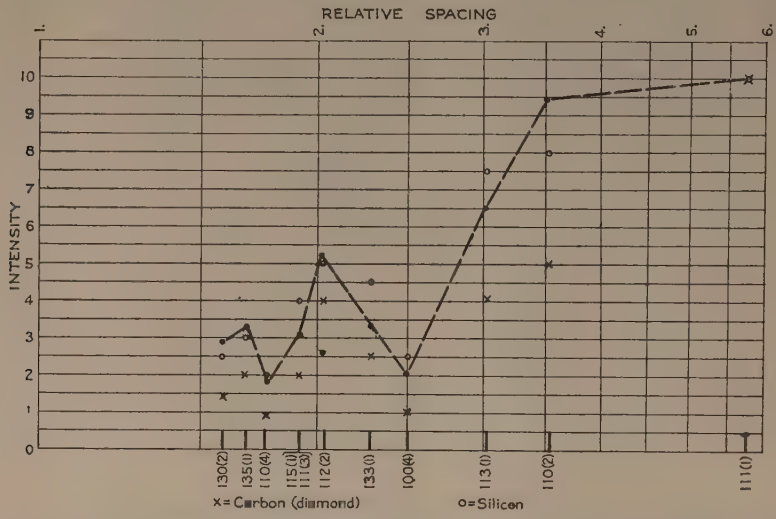


FIG. 154.—The calculated relative intensities of the principal powder reflections from the diamond cubic arrangement [8f], are connected by the dashed lines of this figure. The observed relative intensities of powder lines of carbon (as diamond) and silicon are shown by the crosses and open circles.

ments have been suggested. One (*1916*, 5; *1917*, 5) is a rhombohedral structure of considerable complexity; other powder data (*1917*, 9; *1922*, 46) are held to contradict this grouping and to yield an atomic arrangement which is hexagonal. It is essential not only that this disagreement be removed but that an adequate treatment based upon the results of space group theory be offered before any structure can be accepted for graphite.

The more or less complete graphite patterns (*1922*, 6) that are obtained with "amorphous" carbon from many different sources will be discussed in Chapter XIV.

Silicon.—Several statements of structure, all based upon powder data, give silicon the diamond arrangement [8f]. The lines of these photographs are the ones to be expected from [8f] (Figure 153); their observed intensities are in excellent accord with the intensities calculated for it through the

use of expressions (26) and (33) (Figure 154). These studies yield the following values for a_0, the length of the edge of the unit cube: 5.46A° (*1916*, 5); 5.41A° (*1922*, 37); 5.40A° (*1921*, 46) and 5.43A° (*1917*, 8, 9). Powder reflections show that specimens of "amorphous" silicon are crystalline with this same diamond arrangement (*1916*, 5; *1922*, 37). Thus whereas the graphite structure, whatever it may be, is the usual one for carbon, it has never been found for silicon.

The First Sub-group Elements.—Powder data, as yet unpublished except for one study of thorium, have been made the basis of structure assignments to the elements titanium, zirconium, cerium and thorium. The first three are said to have the hexagonal structure [d] (Figure 150). The data from thorium are those to be expected from a face centered cubic arrangement [4b] (Figure 148). Cerium is said to have a face centered cubic as well as the close packed hexagonal structure.

Titanium (*1920, 33; 1921, 56*).—The lengths of the edges of the unit prism (Figure 150) are given as: $a_0 = 2.97$A°, $c_0 = 4.72$A°, corresponding to the axial ratio $a : c = 1 : 1.59$. Data are needed before this structure can be properly evaluated.

Zirconium (*1921, 56*).—The dimensions of the unit cell (Figure 150) have been stated to be: $a_0 = 3.23$A°, $c_0 = 5.14$A° corresponding to the axial ratio $a : c = 1 : 1.59$. Experimental data are needed.

Cerium (*1921, 56*).—A close packed hexagonal structure with the following dimensions has been described: $a_0 = 3.65$A°, $c_0 = 5.96$A°, corresponding to the axial ratio $a : c = 1 : 1.62$. There is also supposed to be present a second face centered cubic modification having as length of unit edge: $a_0 = 5.12$A°. It is pointed out, however, that it is not impossible for this apparent dimorphism to be due to the presence of admixed impurities. For this reason it is necessary to defer judgment concerning the probable structure of this metal until more work has been done and until data have appeared.

Thorium.—The lines found in the powder pattern of thorium are those which should arise from the face centered cubic structure [4b]. Their observed intensities (*1920*, 3) are compared in Table III with the intensities calculated for [4b]. Except for a greater decrease of the observed intensities with spacing (due perhaps to the large absorption of thorium for the long wave X-rays used), the correspondence is good. The length of the edge of the unit cube, as deduced from these measurements (*1920*, 3) is $a_0 = 5.12$A°. From another determination, for which no data are yet available (*1921*, 56), the length is said to be $a_0 = 5.04$A°.

TABLE III. INTENSITIES OF POWDER REFLECTIONS FROM THORIUM

INDICES	INTENSITY Observed	Calc. for [4b
111(1)	very strong	10
100(2)	strong	5.4
110(2)	strong	4.7
113(1)	strong	6.5
111(2)	medium	1.9
100(4)	very weak	1.0
133(1)	medium strong	3.3
120 (2)	medium weak	3.2
112(2)	weak	2.6
111(3) } 115(1) }	medium weak	3.1

NOTE: Only the intensities of the copper K-alpha reflections, as the more intense ones, are included in this tabulation.

The Second Sub-group Elements.—Powder observations have been carried out upon all three of these metals—germanium, tin and lead. A single reflection has also been recorded from an octahedral face of a crystal of lead. Gray tin and germanium have the diamond arrangement [8f]; the structure of white tin has not been established with any degree of certainty; and the data from lead are said to fit the face centered cubic structure [4b].

Germanium.—The lines found in a powder photograph of metallic germanium are those that would be obtained from a diamond cubic arrangement of atoms [8f]. As Table IV makes clear the observed intensities

TABLE IV. INTENSITIES OF POWDER REFLECTIONS FROM GERMANIUM

INDICES	INTENSITY Observed	Calc. for [8f]
111(1)	very strong	10
110(2)	strong — very strong	9.4
113(1)	strong — very strong	6.5
100(4)	faint	2.1
133(1)	medium — strong	3.3
112(2)	strong — very strong	5.2
111(3) } 115(1) }	faint	3.0
110(4)	faint	1.8
135(1)	medium — strong	3.3
130(2)	medium	2.9

(*1922*, 54) and those calculated from expressions (26) and (33) are in very good agreement. The length of the edge of the unit cube (Figure 153) as deduced from this powder photograph is $a_0 = 5.61$A°. Another powder measurement (*1922*, 46), concerning which no data have yet been published, is said also to point to a diamond arrangement with $a_0 = 5.63$A°.

Tin.—Gray tin has been given the diamond arrangement (Figure 153) as a result of its powder photographs. According to these measurements (*1918*, 3; *1919*, 8), the length of the edge of the unit cube is $a_0 = 6.46A°$. Similar photographs (*1919*, 8) of white tin have been supposed to show that it is tetragonal with a structure containing three atoms within the unit cell. It has recently been stated (*1923*, 58) that this atomic arrangement is incorrect and another tetragonal grouping has been suggested in its place. No structure of this non-cubic modification of tin can be accepted as probable until an adequate treatment is forthcoming based upon space group results and involving a selection between possible unit cells.

Lead.—Unpublished powder spectrometer measurements from a lead plate (*1923*, 72) are said to show diffraction effects in the positions required by a "face centered" cubic arrangement [4b] (Figure 148) for which $a_0 = 4.983A°$. A spectrometer reflection (*1918*, 31) from a single crystal of lead, to be attributed to an octahedral face, gives $a_0 = 4.91A°$.

The Elements of Group V

The Transition Elements.—Two powder photographs have been made from red phosphorus: one of these [1] showed no lines; the other [2] is said to have resulted in a good crystalline diffraction pattern. Beyond these fragmentary observations no study has been made of these elements.

The First Sub-group Elements.—Powder photographs have been prepared from vanadium and tantalum.

Vanadium (*1922, 46*).—No data have ever been published upon vanadium but its powder lines are said to be in the positions required by a "body centered" cubic arrangement [2a] (Figure 147) for which $a_0 = 3.04A°$.

Tantalum (*1920, 33; 1921, 55*).—Lines in a rather poor photograph of this metal agree in position with those to be anticipated from a "body centered" cubic structure [2a] (Figure 147) with $a_0 = 3.272A°$. Nevertheless the relative intensities of 110(1) and 112(1) conflict seriously (Figure 155) with the demands of this arrangement and more experimental work is needed before the crystal structure of tantalum can be taken as probably established.

The Second Sub-group Elements.—Diffraction observations have been made upon antimony and bismuth, but a treatment capable of determining the atomic arrangement in either of these elements has not yet been carried out.

[1] H. C. Burger, Physica *2*, 121 (1922).
[2] *1923*, 13, footnote on p. 3.

Antimony.—Early spectrometer measurements (*1915*, 4) were thought to give both antimony and bismuth a diamond arrangement distorted along trigonal axes. Two more recent spectrometer studies (*1920*, 36; *1921*, 74), which are supposed to show that this structure is not the correct

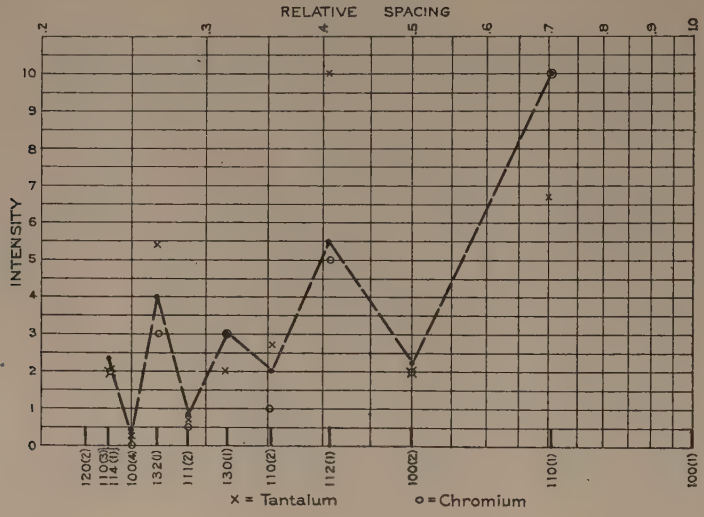


FIG. 155.—In this figure the observed relative intensities of the principal powder lines of tantalum (crosses) and chromium (open circles) are plotted together with the calculated intensities (the points connected by dashed lines) for the "body centered" cubic arrangement, [2a].

one, have been made the basis for a grouping that places eight atoms within the unit cell, four upon a face centered rhombohedral lattice and four more upon a similar lattice obtained by translating the first along the trigonal axis. The amount of this translation is not, however, the same for the two investigations. Much more work, of both an experimental and theoretical character, will be needed before anything definite will be known of the structure of this element.

Bismuth.—Powder observations (*1921*, 60; *1923*, 68) as well as spectrometer measurements (*1915*, 4; *1921*, 74, 59) have been made upon bismuth. It is thought that the recent spectrometer data (*1921*, 74, 59) agree with a rhombohedral structure similar to that proposed for antimony. Powder photographs (*1923*, 68) yield results which are not thought to be in acceptable agreement with the amount of translation deduced from the spectrometer data. A more adequate treatment of bismuth, experimental as well as theoretical, must be carried out before an assignment of structure can be made to its crystals.

The Elements of Group VI

The Transition Elements.—A few spectrometer measurements (*1914*, 4) have been made upon crystals of orthorhombic sulfur. They are, however, in no sense adequate for a determination of atomic or molecular arrangement.

The First Sub-group Elements.—Powder photographs have been prepared from all of these metals except uranium. A body centered cubic arrangement [2a] has been assigned to each element from these data.

Chromium (*1921*, *55*).—The lines in the powder photograph are those given by a "body centered" cubic structure (Figure 147) for which $a_0 = 2.895A°$. As Figure 155 shows there is excellent agreement between the observed intensities and those calculated for this atomic arrangement [2a].

Molybdenum.—The lines in powder photographs of molybdenum have been used to assign it a "body centered" structure [2a]. The length of the

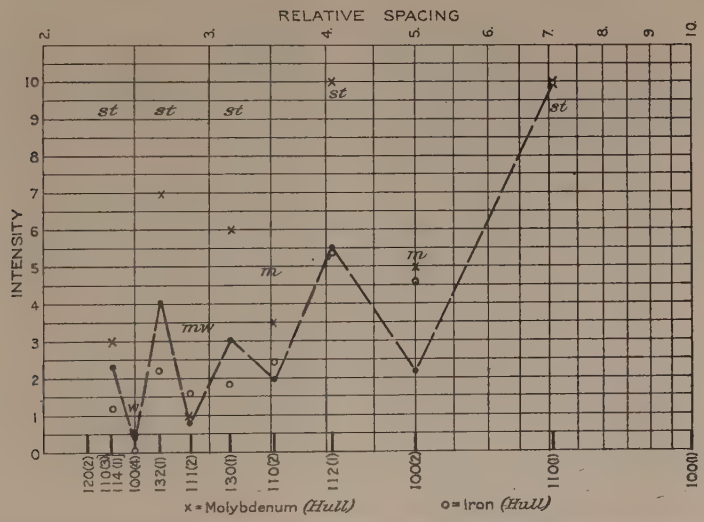


FIG. 156.—The calculated relative intensities of the principal powder reflections from the "body centered" cubic arrangement, [2a], are connected by dashed lines. The observed relative intensities of powder reflections of molybdenum and iron are shown by crosses and open circles. The observed intensities of powder reflections from tungsten are indicated by the letters: st = strong, m = medium, w = weak.

edge of the unit cube containing two atoms (Figure 147) has been stated to be: $a_0 = 3.143A°$ (*1921*, 55) and $a_0 = 3.08A°$ (*1921*, 83). Intensity data (*1921*, 55) for these lines, reproduced in Figure 156, should agree more closely with calculation if [2a] is the correct arrangement.

Tungsten.—Tungsten is reported to give a powder photograph which is practically indistinguishable from that of molybdenum. A comparison photograph of the two leads to the value $a_0 = 3.150$A° (*1921*, 55). From a different study a_0 was found to be 3.18A° (*1917*, 4). The extent to which the observed intensities meet the demands of the "body centered" cubic structure [2a] (Figure 147) is shown in Figure 156 (*1917*, 4); it is none too good.

The Second Sub-group Elements.—No diffraction measurements have been made upon crystals of either selenium or tellurium.

The Elements of Group VII

Metallic manganese has been found to give a powder diffraction pattern which could not be interpreted in terms of any simple atomic arrangement (*1923*, 7, 106). Beyond this observation diffraction effects have not been described from any of the elements of this group.

The Elements of Group VIII

Powder photographs have been made and structures assigned to all of the metals of this group.

Iron.—The powder lines obtained from iron at room temperature are those to be expected from the "body centered" cubic arrangement [2a] of Figure 147. As Figure 156 shows the observed intensities (*1917*, 9) fit well with those calculated for this structure. Determinations of a_0, the length of the edge of the unit cube, yield 2.86A° (*1917*, 9), 2.88A° (*1921*, 88, 89) and 2.872A° (*1923*, 66). Examination of wires at 800° – 830°C (*1921*, 89) seems to prove that the β-form of iron has the same atomic arrangement as the low temperature, α-modification. The γ-iron on the other hand has been made to give at $\pm$ 1000°C (*1921*, 89) five lines in the positions demanded by a "face centered" cubic structure [4b] (Figure 148) for which $a_0 = 3.60$A°. No record has been published of the relative intensities of these lines.

Cobalt (*1919, 18; 1921, 55*).—It is said that powder photographs of cobalt which has been prepared under different physical conditions show that both the hexagonal closest packed grouping [d] (Figure 150) and the "face centered" cubic arrangement [4b] (Figure 148) can coexist at room temperature. Filings of cast cobalt, which by analysis was found to be 99.7% pure, gave only the lines of an hexagonal structure for which $a_0 = 2.514$A°, $c_0 = 4.105$A°, corresponding to the axial ratio $a : c = 1 : 1.633$. Except for an inexplicably weak 10·3(1) reflection, there is satisfactory agreement between observed intensities and those calculated

for this arrangement (Figure 157). After annealing this cobalt in hydrogen at 600°C for six hours, it had developed additional lines about equal

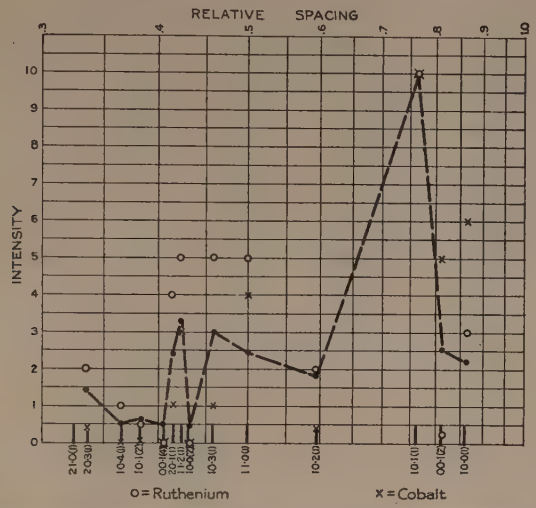


FIG. 157.—The observed relative intensities of the principal powder lines of ruthenium and the hexagonal form of cobalt are plotted as open circles and crosses; the calculated intensities of these reflections for the hexagonal close-packed arrangement, [d], with axial ratio $a : c = 1 : \pm 1.63$ are connected by the dashed lines.

in intensity to the original ones and attributable to a cubic modification. These new lines also were present in cobalt obtained by electrolysis of the sulfate. A sample of cobalt prepared by reducing the oxide in hydrogen at 600°C gave only the lines to be expected from a "face centered" cubic structure [4b] for which $a_0 = 3.554$A°. The individual crystals of this powder were large enough to give separate images upon the film so that intensity observations could be carried out only with difficulty. There is, nevertheless, a serious contradiction (Table V) between the observed intensities and those calculated for [4b]. Until this has been eliminated it is not possible to accept the "face centered" cubic structure [4b] as a probable one for cobalt.

Nickel.—Some early experiments (*1917*, 9) were thought to show that nickel crystallizes sometimes in the "body centered" cubic arrangement [2a] and sometimes with the "face centered" structure [4b]. More recent measurements (*1919*, 18; *1921*, 55; *1920*, 3; *1922*, 99) have found evidence for only the second. The positions of the observed lines and their intensities (Figure 158) are in excellent accord with the requirements of this "face centered" cubic arrangement (Figure 148). The value of a_0 has been variously determined as 3.53A° (*1920*, 3), 3.540A° (*1921*, 55), 3.51A° (*1922*, 99) and 3.510A° (*1923*, 66).

TABLE V. INTENSITIES OF POWDER REFLECTIONS FROM "CUBIC" COBALT

INDICES	INTENSITY	
	Observed	Calc. for [4b]
111(1)	10	10
100(2)	0.8	5.4
110(2)	8.4	4.7
113(1)	10	6.5
111(2)	0.8	1.9
100(4)	0.2	1.0
133(1)	0.4	3.3
120(2)	4.1	3.2
112(2)	0.8	2.6
115(1) } 111(3) }	1.7	3.1
110(4)	0.2	0.9

Ruthenium (*1920, 33; 1921, 55*).—The powder lines from ruthenium are those to be expected from an hexagonal close packed arrangement [d] (Figure 150) for which $a_0 = 2.686A°$, $c_0 = 4.272A°$, corresponding to an axial ratio of a : c = 1 : 1.59. The intensities of these lines are also in good agreement with the demands of this structure (Figure 157).

Rhodium (*1921, 55*).—Rhodium powder yields the lines of a "face centered" cubic arrangement [4b] for which $a_0 = 3.820A°$ (Figure 148). Except for too great a decrease in intensity with spacing, due perhaps to the high density of the metal, the intensities of these lines offer an acceptable fit with this structure (Figure 158).

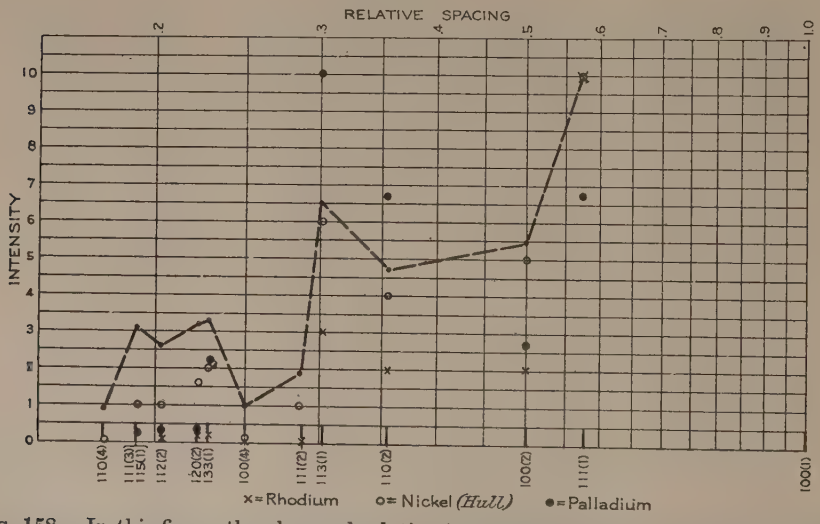


FIG. 158.—In this figure the observed relative intensities of the principal powder lines of rhodium, nickel and palladium are plotted as crosses, open circles and black circles; the calculated intensities of the principal powder lines of the "face centered" cubic arrangement [4b] are connected by the dashed lines.

Palladium.—Palladium gives the powder lines of a "face centered" cubic structure [4b]; their relative intensities (*1920*, 33; *1921*, 55) are, however, in sharp disagreement with the requirements of this atomic arrangement (Figure 158). Two determinations of the length of the edge of the unit cube give $a_0 = 3.950A°$ (*1920*, 33; *1921*, 55) and 3.900A° (*1922*, 64; *1923*, 65). It is essential that this conflict in intensity data be removed before the structure of palladium can be considered as probably known.

Osmium (*1921, 56*).—Powder photographs, concerning which no data have been published, are said to agree with an hexagonal close packed arrangement [d] (Figure 150) for which $a_0 = 2.714A°$ and $c_0 = 4.32A°$. This corresponds to the axial ratio $a : c = 1 : 1.59$.

Iridium.—The lines observed from iridium are those given by a "face centered" cubic arrangement [4b]. As Figure 159 shows there is good

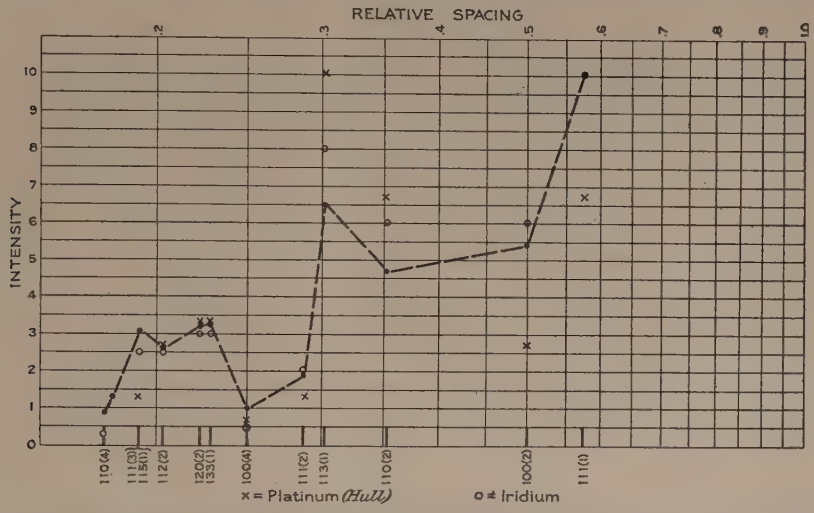


FIG. 159.—The calculated intensities of the principal powder reflections of the "face centered" cubic arrangement [4b] are connected by dashed lines. The observed relative intensities of the important powder lines of platinum and iridium are plotted as crosses and open circles.

agreement of the observed intensities (*1923*, 97) with those demanded by this structure (Figure 148). Two determinations of a_0 give 3.805A° (*1920*, 33; *1921*, 55) and 3.823A° (*1923*, 97); the latter is a comparison measurement made by mixing the sample directly with sodium chloride to serve as a standard.

Platinum.—The lines found in the powder pattern of platinum are those to be expected from a "face centered" cubic arrangement (Figure 148). Two determinations of a_0 give 3.930A° (*1920*, 33; *1921*, 55) and

4.02A° (*1921*, 60). The available intensity data (*1921*, 55) for these lines (Figure 159) are not in sufficiently good agreement with the demands of this structure [4b] so that it can yet be accepted as the probably correct one for platinum.

Summary of Crystal Structure Data for the Elements

The available crystal structure data on the chemical elements have now been reviewed. It is difficult to put a precise valuation upon most of the atomic arrangements given to these crystals. A number of factors contribute to this uncertainty. In the first place the opacity of the metals prevents an optical determination of symmetry properties; and, as zinc and cadmium show, the external appearance of the rather poor crystals of most metals is not necessarily related to their internal structures. There is now abundant evidence to show that, at least when independent knowledge of symmetry is lacking, a consideration of only the positions of powder lines may lead to incorrect crystal structures. For this reason it is necessary to demand that the relative intensities as well as the positions of diffraction effects agree with those calculated from the suggested structure.

The inability to produce other than powder reflections from most metals and the impossibility of obtaining reliable independent knowledge of their symmetry characteristics make their determinations of atomic arrangement the least satisfactory of those from any large group of crystals. In spite of these insufficiencies of the available data it can be concluded that if the elements (only metals and sub-metals are involved) have simple structures, then the atomic arrangements of many of them must be the ones which have been mentioned in the preceding discussions. It is impossible to say how justifiable is this assumption of simplicity: it would be more convincing if none of the metals required a complicated crystal structure.

Inorganic Compounds not Salts

Ferrous Alloys

Iron-Nickel Alloys.—Powder photographs have been prepared of the complete series (*1923*, 66) of solid solutions formed between nickel (Figure 148) and iron (Figure 147). The samples were made by melting Armco iron and electrolytic nickel in an induction furnace, swaging the castings, drawing and rolling out thin tapes. Photographs were taken after four treatments of these specimens: the samples were exposed in (1) without being subjected to additional mechanical or heat treatment, (2) after annealing at 900°–950°C followed by a slow cooling, (3) after an additional heating to 600°C followed by rapid cooling in air, (4) by chilling for a time in liquid air after treatment (2). The results thus obtained are

shown in Figure 160. It will be seen that up to 70% of the nickel atoms in a crystal can be replaced by iron atoms without a change in the structure characteristic of the nickel and with only a comparatively slight change in

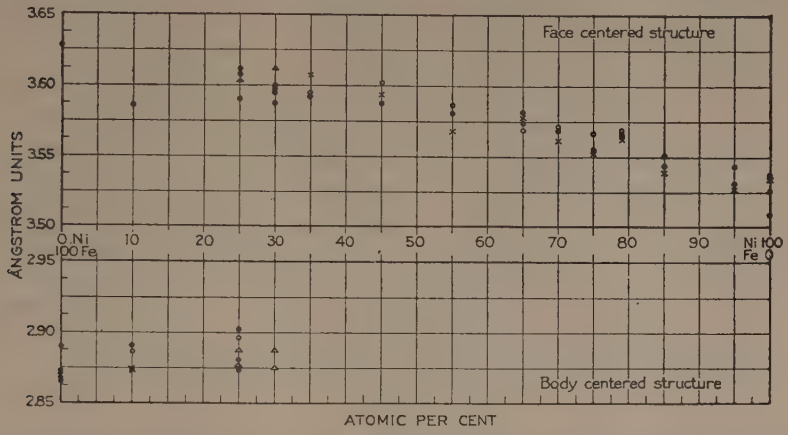


FIG. 160.—A plot showing the variation in length of the edge of the unit cube, a_0, with the composition of iron-nickel alloys. The open circles, black circles, crosses and open triangles refer to alloys subjected to treatments (1), (2), (3) and (4) respectively (see text).

the dimensions of the unit cube. Similarly, alloys from 100% iron to about 25% Ni − 75% Fe are "body centered" like pure iron and possessed of about the same spacings. In the region between ± 25% nickel and ± 30% nickel the two structures coexist. If these alloys [treatment (2)] represent equilibrium states there is thus no sharp break in the series of solid solutions of these two metals which have different atomic arrangements in the pure state. It is not entirely clear what conclusions are to be drawn from the results of the different treatments to which these alloys were subjected. In the main it appears that the cold rolled metals have the largest spacings and that those alloys which have been annealed and subsequently chilled to room temperature (3) give the smallest unit cubes. Furthermore the fact that the "body centered" arrangement persisted only in those 30% nickel alloys which had been held in liquid air suggests that the region of crystal structure inversion would be displaced towards higher percentages of nickel at lower temperatures. This last inference is in keeping with the observation that the "body centered" form is the low temperature modification of iron. It is strengthened by two experiments (*1921*, 6) in which nickel steels each containing about 25% nickel and showing the face centered arrangement developed an admixed body centered grouping after being held for some time in liquid air. This general outline of the structures of iron-nickel alloys and of the range of their

occurrence agrees with previous qualitative experiments (*1921*, 6). No detailed diffraction data have been published for these alloys; with the exception of approximate chemical compositions no numerical data are contained in the first qualitative study (*1921*, 6). It is interesting to note that crystal structure studies give no suggestion of the existence of the intensely magnetic "permalloy." [1]

Iron-Manganese Alloys (*1923*, 7).—Iron and manganese are supposed to form a continuous series of solid solutions. It has been said that for slowly cooled alloys ranging in composition between pure iron and about 20% Mn–80% Fe the atomic arrangement is the body centered one characteristic of α-iron; that alloys containing between 20% and 40% of manganese are mixtures of the "body centered" and "face centered" structures; that they are then purely "face centered" up to about 60% manganese; and that after passing through a short range of mixed "face centered" cubic and pure manganese forms, they are like the latter for the remainder of the composition range. No detailed data have been published upon this alloy series. It has also been found that when a manganese steel containing 12.1% Mn and 1.34% C was quenched in water from 1000°C., it gave the face centered cubic arrangement characteristic of γ-iron; this steel did not develop any evidence for the "body centered" arrangement after being cooled in liquid air (*1922*, 98).

Iron-Cobalt (*1921*, *6*).—Cobalt and iron are supposed to form an unbroken series of solid solutions. Powder photographs show that up to about 80% of the iron atoms can be replaced by cobalt atoms without change in the "body centered" structure of iron. A mixture of "body" and "face" centered forms has been found in the region between 80% and 90% cobalt. Above this only the "face centered" modification is present until at about 98% cobalt the hexagonal arrangement which supposedly coexists with the face centered cubic one in pure cobalt begins to make its appearance. No numerical data accompany this account of structure.

Other Ferrous Alloys (*1923*, 7).—A few observations, unaccompanied by numerical data, have been recorded upon the system iron-chromium. It has also been said that there is little (if any) solid solution between iron and either tungsten or molybdenum; but there is the formation of a compound.

Non-ferrous Alloys

Silver-Gold.—Gold and silver both have a "face centered" cubic arrangement (Figure 148) with very nearly the same values for a_0: 4.080A° and 4.075A°. They form a complete series of solid solutions. As a result of one study (*1923*, 7), upon which no data have appeared, it is said that

[1] H. D. Arnold and G. W. Elmen, Jour. Frankl. Inst. *195*, 621 (1923).

no deviation can be detected from a linear proportionality between composition and size of the unit cell. In another examination (*1922*, 63) abnormally high spacings (Figure 161) were found for annealed alloys

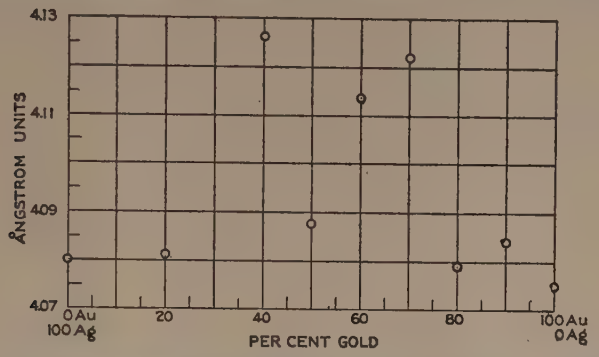


FIG. 161.—A plot showing the observed variation of the length of the edge of the unit cube, a_0, with composition for a series of gold-silver alloys.

of the compositions Ag_3Au_2, Ag_2Au_3 and Ag_3Au_7. More work is obviously required to provide explanations for such abnormalities.

Silver-Palladium (*1922*, *63*).—Silver and palladium are "face centered" cubic (Figure 148) with similar values for a_0 : 4.080A° and 3.900A°. The continuous series of solid solutions formed by these metals have spacings somewhat too small to yield a linear proportionality with composition (Figure 162).

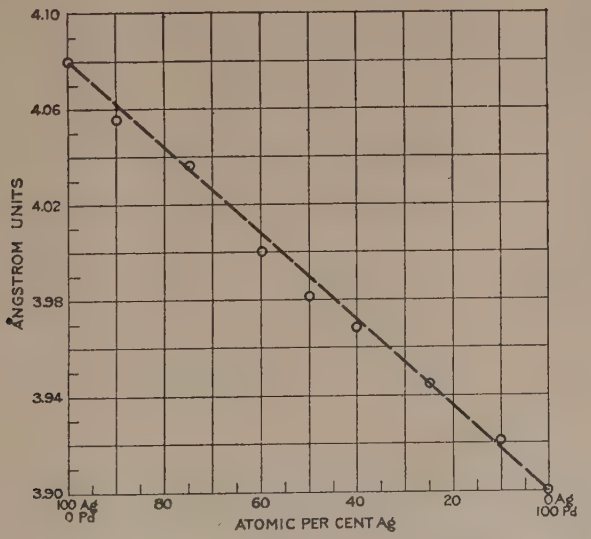


FIG. 162.—A plot showing the variation of the length of the edge of the unit cube, a_0, with composition for silver-palladium alloys.

Gold-Copper (*1922, 52; 1923, 7*). Gold and copper likewise have "face centered" cubic structures and form a continuous series of solid solutions. The sizes of their unit cells are, however, quite different and the dimensions of their solutions apparently deviate largely from a linear relationship with composition (Figure 163). It has been stated (*1923*, 7) that powder

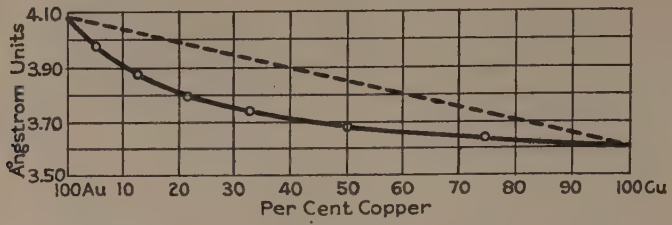


FIG. 163.—A plot showing the variation of the size of the unit cube (expressed in lengths a_0) with the composition of copper-gold alloys (after Bain).

photographs of alloys of such special compositions as $AuCu_3$ or Au_3Cu give evidence for the existence of a regular distribution of one kind of atom with respect to the other. Unfortunately no data bearing upon this point have yet been published.

Copper-Zinc (*1921, 6; 1923, 7*).—The available results on a series of brasses are shown in Table VI. There is moderate agreement with the diagram as deduced by thermal analysis.

TABLE VI. DIFFRACTION DATA UPON COPPER-ZINC ALLOYS

Composition % Zinc	Type of Diffraction Pattern
0 (100% Cu)	Face centered cubic (a_0 = ± 3.60A°)
20	" " "
31	" " " (a_0 = ± 3.68A°)
37	" " "
47	Mixture of face centered and body centered
50	Body centered cubic
63	" " "
69	Mixture (?)
79	Rhombohedral (?)
82	"
90	Mixture rhombohedral (?) and hexagonal
94	" " "
100 (0% Cu)	Hexagonal

Copper-Nickel (*1923, 7*).—These two metals, both showing the "face centered" cubic structure (Figure 148) are supposed to form a continuous series of solid solutions. Their diffraction patterns have been reported to confirm this.

Molybdenum-Tungsten (*1923*, *7*).—It has been reported that these two metals, with the same "body centered" cubic arrangements and practically identical values of a_0, form a continuous and unbroken series of solid solutions.

Heussler Alloys (*1923*, *106*).—Powder photographs have been made from two Heussler alloys of the following compositions:

Alloy IVa—15.9% Al; 23.9% Mn; 60.3% Cu.
" IIIa—14.3% Al; 28.6% Mn; 57.1% Cu.

Alloy IIIa is said to show only the pattern of a "face centered" cube for which $a_0 = 3.70A°$; the other is supposed to give this same pattern and more faintly the lines of a "body centered" cubic arrangement for which $a_0 = 2.98A°$. Aside from reproductions of the photographs no diffraction data are published for these alloys.

The same diffraction effects were obtained with the alloys in and out of a strong magnetic field.

Other Non-Ferrous Alloys (*1923*, *7*).—Several isolated alloys, representative of systems of limited miscibility, have been examined. In all of these instances the change in volumes of the crystals on solution of the second metal is less than would be expected from a simple mixing of the two metals. A 94.98% copper—5.02% tin (atomic percents) alloy has a length of edge of the unit "face centered" cube of 3.655A°, as contrasted with 3.60A° for pure copper. When 18.8 atomic percents of aluminum replace copper atoms the length a_0 becomes 3.633A°. Some alloys of copper and manganese exhibit the copper structure; others show the atomic arrangement of manganese. An alloy of two thirds copper atoms and one third manganese atoms is still face centered cubic like copper and gives $a_0 = 3.615A°$. Numerical data have not been given for any of these cases.

Solid Solutions of Hydrogen in Palladium.—Two conflicting studies have been published on the effect of the occlusion of hydrogen upon the crystal structure of palladium. In one investigation (*1923*, 104) it was found that palladium maintains its own crystal structure and swells its dimensions by an amount which is determined by the amount of the dissolved hydrogen. A sample which had taken up 660 times its own volume of hydrogen, and thus contained 29 molecular percents of hydrogen, was found to have a value of a_0 2.8% greater than that for pure palladium.

As a result of the other more complete study (*1923*, 65) it is found that palladium does not continuously absorb hydrogen but that as soon as some gas has been occluded a second phase which may be interpreted as a sort of saturated solution of hydrogen in individual palladium crystals

makes its appearance. In other words, as soon as a single crystal of palladium has started to absorb hydrogen it can continue to do so up to its saturation point more easily than a new crystal can begin absorbing. The two patterns showed the same planar reflections, that of the solution differing only in having somewhat larger spacings. The dimensions of this larger unit were not constant but varied between $a_0 = 4.000A°$ and 4.039A°; when the solution pattern was intense, however, a_0 was never lower than 4.023A°. An attempt was made to define the positions of the hydrogen atoms on the assumption that the saturated crystals are those of an earlier proposed hydride Pd_2H. The absence of direct evidence for the existence of this compound and especially the observed variability of a_0 make it seem more natural to consider the larger crystals as merely more or less saturated solutions of hydrogen in palladium.

Additional experiments are needed to remove the apparent conflict between the results of these two studies of the system palladium-hydrogen.

Iridosmium (1921, 4). — The crystal structure of a natural alloy of iridium and osmium has been studied with Laue photographs. Iridium is face centered cubic (Figure 148) and osmium probably is hexagonal close-packed (Figure 150) and it is probable that their alloys exhibit a series of solid solutions which like the alloys of nickel with cobalt are partly hexagonal and partly cubic. The Laue photographs show that the alloy used in this investigation had hexagonal symmetry. Unfortunately its composition was not determined. The Laue photographs were prepared with such a voltage impressed upon the tube that the shortest reflected wave length, as determined from a photograph of potassium chloride, was about 0.18A°. By assigning a crystallographically possible set of indices to these Laue spots and calculating therefrom the wave lengths of the reflected X-rays, fair agreement was found between the observed low wave length limit and the requirements of an hexagonal unit cell containing two atoms and having an axial ratio of $a : c = 1 : 1.590 \pm 0.005$. In view of the strong absorption of the iridium and osmium atoms this agreement has been considered sufficient to establish the two-atom cell as the probably correct one; more conclusive evidence upon this point is, however, to be desired. By the procedure outlined in discussing the structure of magnesium (page 237) arrangement [d] (Figure 150) is shown to be the only one which fits the diffraction data if the crystals examined are untwinned and if this two-atom unit is the correct one.

Summary

It will be seen from the preceding review that with a few exceptions most of the work yet done upon alloys and intermetallic compounds is fragmentary and reported in such meager detail as to be of uncertain value

to crystal analysis. A study of alloys is of great importance because of the possibility it offers of throwing light upon the problems of solid solutions and their relations to their associated chemical compounds. Perhaps the two most important results yet attained in the study of alloys are the proofs (1) that the spacings in a series of solid solutions of two isomorphous metals (copper and gold, for instance) do not necessarily follow a straight line relation, and (2) that a series of solid solutions with end members of different structures may appear continuous and unbroken through the coexistence over a certain range of compositions of two different arrangements in varying amounts (the nickel-iron series, for example).

Satisfactory deductions of atomic arrangements for intermetallic compounds will be exceedingly difficult with existing methods. Their opacities and the problems of preparing large single crystals make them subject to all the limitations of studies of the pure metals; and for intermetallic compounds an application of the (at best doubtful) hypothesis of probable simplicity in atomic arrangement is no longer justifiable.

Chapter XI. The Structures of Carbides, Oxides, Sulfides, etc.

Carbides

Carborundum, CSi.—The symmetry and crystal structure of carborundum present an interesting and puzzling problem for which there is not as yet a satisfactory answer. In the past it has been supposed that CSi crystallizes in the rhombohedral division of the hexagonal system, the rhombohedral angle being almost 90°. On the basis of studies[1] of face development it has recently been concluded, however, that three distinct modifications exist, all with practically identical axial ratios and all crystallizing in the hexagonal system. Laue photographs which are strong evidence for their separate existence have been prepared (*1920*, 30) from crystals belonging to these three supposed types; their tracings are shown in Figure 164.

FIG. 164.—Tracings of basal Laue photographs of the three types of carborundum (after Hauer and Koller).

Three separate studies have been made of the diffraction effects from carborundum. Two of them—one of which used spectrometer measurements (*1918*, 9), the other, powder photographs (*1920*, 32)—did not take into consideration this polymorphism and were not reinforced by either optical data or crystallographic measurements. Since these modifications frequently intergrow and twinning is very common, it would be impossible to attach any certainty to the results of either of these studies. The spectrometer observations (*1918*, 9) were thought to establish a distorted diamond arrangement in which half the carbon atoms were replaced by

[1] H. Baumhauer, Zeit. f. Krist. *50*, 33 (1912); *55*, 249 (1915–20).

silicon atoms. A Laue photograph published elsewhere [1] by one of the authors of that study was of such a character that it could not have agreed with this structure (unless the crystal producing it were twinned). It was afterwards asserted (*1919*, 17), though no data have ever appeared, that these data agree with an undistorted diamond arrangement. Powder photographs (*1920*, 32), measurements upon which also have never been published, were thought to show lines of both the hexagonal and the cubic close packings; this was imagined to mean that carborundum crystals consist of a combination of these two arrangements.

In view of present knowledge the third investigation (*1921*, 38) is the only one which can be given weight. This study was made upon crystals of the second Baumhauer type using spectrum and Laue photographs. Its data are considered to show that the unit cell is an hexagonal one containing 24 molecules of CSi. A structure based upon this unit seems to be in moderate agreement with the Laue data. The discussion which accompanies this determination of structure does not prove that the chosen unit is the simplest possible one; it is therefore desirable that further work be carried out before this atomic arrangement is definitely accepted. It is also stated that the other two types (I and III) have unit cells containing 24 molecules.

Oxides

Monoxides of the Univalent Elements

Ice, H_2O.—Ice is usually assigned to the hexagonal division of the hexagonal system though some observations have been thought to make a trigonal symmetry probable. A Laue photograph (*1917*, 18) from an ice crystal exhibited complete hexagonal symmetry and yielded an axial ratio of a : c = 1 : 1.678. By proceeding from the assumption that this crystal was not twinned, the few spots on its photograph have been found to be compatible (*1919*, 14) with a unit cell containing two molecules of H_2O and having $a_0 = 3.46A^\circ$ and $c_0 = 5.53A^\circ$ (a : c = 1 : 1.60). Some spectrometric measurements (*1918*, 22) have led to a unit containing four molecules of H_2O and giving $a_0 = 4.74A^\circ$ and $c_0 = 6.65A^\circ$ (a : c = 1 : 1.4026). Powder photographs from ice (*1921*, 35) that was made by plunging a small glass tube of water into liquid air have been imagined to display the lines of an hexagonal "close-packed" arrangement with an axial ratio of a : c = 1 : 1.62. The unit cell of this structure, which also contains four molecules, is given the dimensions $a_0 = 4.52A^\circ$ and $c_0 = 7.32A^\circ$. Another structure (*1922*, 15), in approximate agreement with the powder measurements, has been proposed besides the three atomic arrangements suggested directly for these unit cells.

[1] In A. E. H. Tutton, Crystallography and Practical Crystal Measurement, Vol. i, p. 689 (London, 1922).

The sets of axes of these units are not merely rotations of one another through angles of 30° or integral multiples of one another; there is consequently a serious conflict among the reported experimental data on ice. Because of the danger of twinning in the crystals used in making both the Laue photographs and the spectrometer measurements, the powder data are the most reliable. These data alone are probably insufficient to establish the structure of ice; consequently nothing definite can be considered as known about its atomic arrangement.

Lithium Oxide, Li_2O (1923, 13, footnote, p. 23).—It is said that powder photographic data from Li_2O probably lead to a calcium fluoride arrangement [4b, 8e] (Figure 171) for which the length of the edge of the unit cube is $a_0 = 4.62A°$. No diffraction data have yet been published.

Cuprite, Cu_2O.—Optical examination as well as crystallographic study shows cuprite to have cubic symmetry. Its etch figures are holohedral but there is one record of a rare face development supposed to indicate that it belongs to the enantiomorphic hemihedral class.

Spectrometer measurements (*1915*, 4, p. 155), which have only been reported in a rough graphical form, give a value of $m/n^3 = 2$; from them $a_0 = 4.32A°$ (approximately) if $m = 2$. A powder photograph (*1922*, 68) shows no reflections requiring a unit larger than one yielding $m = 2$.

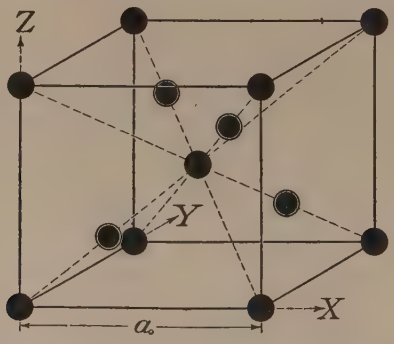


FIG. 165.—The unit cell of the "cuprite arrangement" [2a, 4d]. Copper atoms, in arrangement [4d], are designated by the ringed circles; oxygen atoms, in arrangement [2a], appear as the full circles.

If it is assumed that the two oxygen atoms within a unit cube are alike, then reference to a tabulation (*1922*, 111) of the special cases of the cubic space groups proves that only the following atomic arrangement (Figure 165) is possible:

Copper atoms: $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}\frac{3}{4}$; $\frac{3}{4}\frac{1}{4}\frac{3}{4}$; $\frac{3}{4}\frac{3}{4}\frac{1}{4}$,
Oxygen atoms: 000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. [2a, 4d]

This structure can be derived from Ti−2, O−2 and Oi−4.

Its correctness for cuprite can be checked by calculating the relative intensities of the principal powder reflections through expression (26):

When n is odd: . . . . . (34)

If the indices are two odd and one even, $A = 2\bar{O}$, $B = 0$;
If the indices are two even and one odd, $A = B = 0$;
If the indices are all odd, $A = 0$, $B = \pm 4\,\overline{Cu}$;

When n is even:

If the indices are two odd and one even, $A = 2\bar{O} + 4\overline{Cu}$, $B = 0$;
If the indices are two even and one odd, or all odd,
$A = 2\bar{O} \pm 4\overline{Cu}$, —when n = 2, 6, etc., + when n = 4, 8, etc.,
$B = 0$ always.

These values for A and B used in (26) lead to the calculated intensities of Table I if $\bar{O}$ and $\overline{Cu}$ are taken equal to eight and 29 (the atomic numbers

TABLE I. INTENSITIES OF POWDER REFLECTIONS FROM CUPRITE (Cu_2O)

INDICES	INTENSITY Calc. for [2a, 4d]	Observed
100(1)	0	absent
110(1)	0.5	weak—very weak
111(1)	10	very very strong
100(2)	4	strong
120(1)	0	absent
112(1)	0.3	trace
110(2)	6.1	very strong
001(3), 122(1)	0	very very weak (probably due to β-line of 113(1))
130(1)	0.2 —	trace
113(1)	6.5	strong — very strong
111(2)	1.5	medium-weak

of oxygen and copper). They are in excellent agreement with the observed intensities (*1922*, 68) of corresponding reflections.

If the improbable assumption were made that the two oxygen atoms can be different from one another (even though all four copper atoms are alike), the following possible arrangement can be deduced from T—1 and Te—1:

Copper atoms: uuu; uūū; ūuū; ūūu.
Oxygen atoms: 000; and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

This structure is indistinguishable from the preceding one [2a, 4d] if $u = \frac{1}{4}$; and any detectable deviation from $u = \frac{1}{4}$ would be accompanied by the appearance of other lines than those arising from arrangement [2a, 4d]. A line found in the position of 001(3) and 221(1) is probably a K-beta

reflection by 113(1); otherwise there is no evidence for such additional reflections.

It consequently must be concluded that if the structure of cuprous oxide is simple, as all the available evidence indicates, its atomic arrangement must be that of [2a, 4d]. The best determination of the length of the edge of the unit cube (Figure 165) is $a_0 = 4.26A°$ (*1922*, 68).

Silver Oxide, Ag_2O.—Silver oxide is known to crystallize in octahedrons which are optically isotropic; its cubic symmetry is thus definitely established. The sines of the angles of reflection for the four most conspicuous lines in a powder photograph (*1922*, 103) of Ag_2O are recorded in column (1) of Table II. It has been shown (page 189) that for a cubic crystal the ratio of the sine-squares of planar reflections are those of small whole numbers. The values of these sine-squares (for the K-alpha line of molybdenum) are shown in column (2) of Table II. Trial proves that their ratios are those of the numbers of column (3) which are close approaches to the integers of column (4). From reference to Table III of Chapter VI it is clear that these reflections must therefore be due to the planes of column (5) of Table II. It then follows from the use of one of

Table II. Powder Data upon the Four Strongest Lines of Silver Oxide (Molybdenum K-α Radiation)

$\sin\theta$	$\sin^2\theta$	Ratios of $\sin^2\theta$	$(h^2+k^2+l^2)n^2$	Indices
0.129	.0166	3	3	111(1)
.149	.0221	3.99	4	100(2)
.212	.0448	8.09	8	110(2)
.249	.0620	11.18	11	113(1)

these powder reflections (thus identified) in expression (29a) that m/n^3 must equal two. Additional powder photographic results (*1922*, 68) yield no reflections requiring that m be greater than two. The problem of choosing the correct atomic arrangement is thus identical with that for cuprous oxide. There is satisfactory agreement between observed intensities of the principal powder reflections and those calculated for the cuprite arrangement [2a, 4d] by expression (26) (Table III).

It is thus necessary to conclude that if the atomic arrangement of silver oxide is simple, as all the data indicate, it must be that of [2a, 4d]. The two available sets of powder data were from photographs in which the lines were unusually broad; they give for this unit cell (Figure 165) $a_0 = 4.77A°$ (*1922*, 103) and $4.718A°$ (*1922*, 68). Approximate corrections for the size of the cylindrical specimen were made in deducing this second value; the first was obtained from a thin film of powder which did not require the same corrections. Another powder photograph (*1922*, 27), for which no data have ever been published, is said to lead to $a_0 = 4.69A°$.

TABLE III. INTENSITIES OF POWDER REFLECTIONS FROM SILVER OXIDE (Ag_2O)

INDICES	Calc. for [2a, 4d]	INTENSITIES Observed (*1922*, 103)	Observed (*1922*, 68)
100(1)	0	0	absent
110(1)	0.2	0	very very weak
111(1)	10	10	strong
100(2)	4.5	7	strong (broad)
120(1)	0	0	absent
112(1)	0.1	0	very weak (washed out)
110(2)	5.6	7	strong
001(3) } 122(1) }	0	0	very very weak (probably β of 113(1))
130(1)	0.05	0	trace
113(1)	6.5	6	strong
111(2)	1.6	—	medium-weak

Monoxides of the Divalent Metals.—Especially detailed investigations have been carried out upon the structures of magnesium oxide and zinc oxide. All the monoxides that have been studied are like one or the other of these two with the exception of the triclinic cupric oxide. It will consequently be convenient to discuss magnesium and zinc oxides before proceeding to the less studied crystals isomorphous with them.

Cupric Oxide, CuO.—Two powder photographs (*1922*, 43, 68) have been made from CuO. As a result of a lengthy treatment of one of them

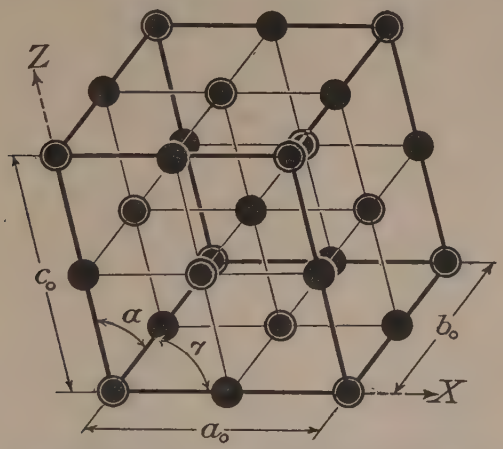


FIG. 166.—The unit cell of a possible arrangement of the atoms in crystals of cupric oxide (CuO). The ringed circles can represent either the copper or the oxygen atoms.

(*1922*, 68) a triclinic structure is suggested which resembles sodium chloride and has the following dimensions (Figure 166):

$$a_0 = 3.74\text{A}^\circ;\ b_0 = 4.67\text{A}^\circ;\ c_0 = 4.67\text{A}^\circ,$$
$$\alpha = 85^\circ 21';\ \beta = 86^\circ 25';\ \gamma = 93^\circ 35'.$$

The powder data do not seem sufficient to prove the correctness of this proposed atomic arrangement.

Magnesium Oxide, MgO (1919, 20; 1920, 19; 1921, 46, 47, 80, 94; 1922, 36, 43).—Reflections from individual crystal faces, Laue photographs and powder photographs have all been obtained from magnesium oxide. Its optical behavior leaves no doubt of its cubic symmetry. A reflection spectrum photograph taken with (100) as the principal reflecting face shows that $m/n^3 = 4$. No data have been found either from interpretation of the Laue photographs or on powder photographs which require that m should be greater than four. From the few crystallographic measurements available there is no evidence that the symmetry of MgO is less than holohedral. If, however, for the sake of completeness all cubic space groups are considered, the following atomic arrangements are found (*1921*, 94) to be possible. In deducing them no limiting assumptions are necessary concerning the equivalence of chemically like atoms.

[4g, 4h]	Mg atoms:	$000;\ \frac{1}{2}\frac{1}{4}\frac{3}{4};\ \frac{3}{4}\frac{1}{2}\frac{1}{4};\ \frac{1}{4}\frac{3}{4}\frac{1}{2},$
	O atoms:	$\frac{1}{2}\frac{1}{4}\frac{1}{4};\ 0\frac{3}{4}\frac{1}{4};\ \frac{1}{4}0\frac{3}{4};\ \frac{3}{4}\frac{1}{4}0.$
[4j, 4i]	Mg atoms:	$000;\ \frac{3}{4}\frac{1}{4}\frac{1}{2};\ \frac{1}{4}\frac{1}{2}\frac{3}{4};\ \frac{1}{2}\frac{3}{4}\frac{1}{4},$
	O atoms:	$\frac{1}{2}\frac{1}{2}\frac{1}{2};\ 0\frac{1}{4}\frac{3}{4};\ \frac{3}{4}0\frac{1}{4};\ \frac{1}{4}\frac{3}{4}0.$
[4b, 4c]	Mg atoms:	$000;\ \frac{1}{2}\frac{1}{2}0;\ \frac{1}{2}0\frac{1}{2};\ 0\frac{1}{2}\frac{1}{2},$
	O atoms:	$\frac{1}{2}\frac{1}{2}\frac{1}{2};\ 00\frac{1}{2};\ 0\frac{1}{2}0;\ \frac{1}{2}00.$
[4b, 4d]	Mg atoms:	$000;\ \frac{1}{2}\frac{1}{2}0;\ \frac{1}{2}0\frac{1}{2};\ 0\frac{1}{2}\frac{1}{2},$
	O atoms:	$\frac{1}{4}\frac{1}{4}\frac{1}{4};\ \frac{3}{4}\frac{3}{4}\frac{1}{4};\ \frac{3}{4}\frac{1}{4}\frac{3}{4};\ \frac{1}{4}\frac{3}{4}\frac{3}{4}.$
[4a]	Mg atoms:	uuu; uūū; ūuū; ūūu,
	O atoms:	a similar term in u′.
[4f]	Mg atoms:	uuu; $u + \frac{1}{2}, \frac{1}{2} - u, \bar{u}$; $\bar{u}, u + \frac{1}{2}, \frac{1}{2} - u$; $\frac{1}{2} - u,$ $\bar{u}, u + \frac{1}{2},$
	O atoms:	a similar term in u′.
[1a, 3b; 1b, 3a]	Mg atoms:	000 and $00\frac{1}{2}$; $0\frac{1}{2}0$; $\frac{1}{2}00,$
	O atoms:	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}.$

A study of the Laue photographic and powder photographic data shows that only planes with all odd indices give first order reflections. A calculation (see page 215) of the A and B terms of the intensity expression (20) indicates that arrangements [4g, 4h] and [4j, 4i] should give odd order effects from planes with two odd and one even indices; since these are not found [4g, 4h] and [4j, 4i] are impossible as structures for MgO. In arrangement [1a, 3b; 1b, 3a] reflections with two even and one odd indices, as well as those with all odd indices, should appear in the first order region; it is therefore to be eliminated from further consideration. It can also be shown that [4a] and [4f] do not satisfy the experimental requirement of only all odd reflections in the first order unless they approach

indistinguishably close to either [4b, 4c] or [4b, 4d]. The choice of the correct arrangement thus lies between [4b, 4c] and [4b, 4d].

The A and B terms of expression (20) have for [4b, 4c] the following values:

When n is odd:

If the indices are all odd, $A = 4\overline{Mg} - 4\overline{O}$, $B = 0$;
If the indices are two even and one odd or two odd and one even, $A = B = 0$;

When n is even:

$A = 4\overline{Mg} + 4\overline{O}$, $B = 0$, always. (35)

The values of A and B for [4b, 4d] are as follows:

When n is odd:

If the indices are all odd, $A = 4\overline{Mg}$, $B = 4\overline{O}$;
If the indices are two odd and one even or two even and one odd, $A = B = 0$;

When n is 2, 6, etc.:

If the indices are all odd or two even and one odd, $A = 4\overline{Mg} - 4\overline{O}$, $B = 0$;
If the indices are two odd and one even, $A = 4\overline{Mg} + 4\overline{O}$, $B = 0$;

When n is 4, 8, etc.:

$A = 4\overline{Mg} + 4\overline{O}$, $B = 0$ always. (36)

The characteristic differences between the diffraction effects from these two structures thus lie in the relatively greater intensity of odd order reflections from [4b, 4d] and in the comparative weakness of its two even and one odd and all odd reflections when n = 2, 6, etc. It is always possible to distinguish between [4b, 4c] and [4b, 4d] as long as the scattering power of one kind of atom in the crystal is not insignificant compared with that of the other. For this choice, powder photographic comparisons of first and second order reflections are most valuable.

In Table IV the observed intensities of powder reflections from MgO are compared with those calculated by the application of (35) and (36) in expression (26). Magnesium and oxygen have atomic numbers so close together that the relative intensities of calculated reflections will be largely influenced by the particular values chosen for the scattering powers of these atoms. From a number of sources it seems probable that the

TABLE IV. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS OF MgO ($\overline{Mg} = 12$; $\overline{O} = 8$)

INDICES	INTENSITIES		
	Observed	Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	2	0.75	10
100(2)	10	10	0.4
110(2)	9	8.8	9.1
113(1)	2	0.5	6.5
111(2)	5	3.6	0.1
100(4)	3	1.9	2.0
133(1)	0.5	0.25	3.3
120(2)	6	6.0	0.2
112(2)	5	4.9	5.0

atoms of MgO are doubly charged ions. If such is the case the electron number of each atom in this crystal is ten; if then an exact proportionality existed between the numbers of electrons in an atom and its scattering power, no first order reflections would be found from any planes. Some powder photographs have failed to show the presence of such reflections (*1921*, 47) but they are clearly observable in the negative from which Figure 137a was printed, and though faint are present in the Laue photographs (*1921*, 94). There is nevertheless good agreement between calculations for arrangement [4b, 4c], the sodium chloride arrangement (Figure

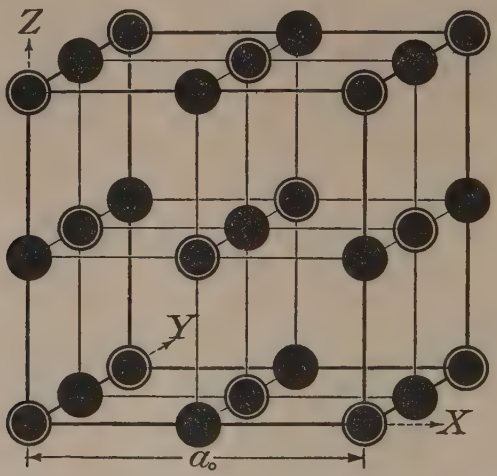


FIG. 167.—The unit cube of the "sodium chloride arrangement" [4b, 4c]. Either the sodium or the chlorine atoms can be represented by the ringed circles.

167), and observed intensities of reflection. It is thus clear that either this structure or an indistinguishably close approach to it must be the correct one for magnesium oxide.

Estimates of the length of the edge of the unit cube for magnesium oxide have varied from 4.22 ± 0.02A° to 4.18A°; the most probable value seems to lie around 4.20A°.

Zincite, ZnO.—Crystals of zinc oxide are usually assigned to the hemimorphic hemihedral class, 6e, of the hexagonal system. Spectrometer measurements from single crystal faces (*1915*, 4, p. 227; *1920*, 11), Laue photographic data (*1921*, 4) and powder photographs (*1922*, 5, 43, 95) are all available for ZnO. A Laue photograph (*1921*, 4) taken with the X-rays normal to the basal, (00·1), face shows complete hexagonal symmetry and thus does not conflict with the assumption that zincite has the symmetry of the point group 6e. From this photograph and a knowledge of the minimum wave length producing its spots, it is shown that the existing diffraction data agree with an hexagonal unit prism having the axial ratio a : c = 1 : 1.608 and containing two molecules of ZnO. It is considered that the following three arrangements (*1916*, 8; *1921*, 4), all based upon special cases of the space group 6e−4, are the only hemimorphic ones compatible with the general requirements of the Laue photographic results:

[e] Zinc atoms: $\frac{1}{3}\frac{2}{3}u$; $\frac{2}{3}$, $\frac{1}{3}$, $u + \frac{1}{2}$;
Oxygen atoms: $\frac{1}{3}\frac{2}{3}v$; $\frac{2}{3}$, $\frac{1}{3}$, $v + \frac{1}{2}$.

On transferring the origin to the point $(\frac{1}{3}, \frac{2}{3}, u + \frac{1}{2})$ this becomes:

[e′] Zinc atoms: 000; $\frac{2}{3}\ \frac{1}{3}\ \frac{1}{2}$,
Oxygen atoms: 00v; $\frac{2}{3}$, $\frac{1}{3}$, $v + \frac{1}{2}$.
[f] Zinc atoms: $\frac{1}{3}\frac{2}{3}0$; $\frac{2}{3}\frac{1}{3}\frac{1}{2}$,
Oxygen atoms: 00v; 0, 0, $v + \frac{1}{2}$.
[g] Zinc atoms: 00v; 0, 0, $v + \frac{1}{2}$,
Oxygen atoms: $\frac{1}{3}\frac{2}{3}0$; $\frac{2}{3}\frac{1}{3}\frac{1}{2}$.

Arrangement [g] differs from [f] only in the interchange of the positions of the zinc and oxygen atoms.

The A and B terms of intensity expression (20) have the following forms for [e′]:

$$\left.\begin{aligned} A &= \overline{Zn}[1 + \cos 2\pi n(\tfrac{2}{3}h + \tfrac{1}{3}k + \tfrac{1}{2}l)] + \overline{O}[\cos 2\pi nvl \\ &\quad + \cos 2\pi n(\tfrac{2}{3}h + \tfrac{1}{3}k + vl + \tfrac{1}{2}l)]; \\ B &= \overline{Zn}[\sin 2\pi n(\tfrac{2}{3}h + \tfrac{1}{3}k + \tfrac{1}{2}l)] + \overline{O}[\sin 2\pi nvl \\ &\quad + \sin 2\pi n(\tfrac{2}{3}h + \tfrac{1}{3}k + vl + \tfrac{1}{2}l)]. \end{aligned}\right\} \quad (37)$$

It will be seen to be a property of this structure that I = 0 for odd order reflections with the indices hk·(2m + 1), where 2h + k = 3p and m and p can be any integers including zero. As the analogous expressions would make clear, the same reflections are absent from structures built

upon [f] and [g]. Admitting the correctness of the analysis up to this point, two questions remain to be settled: One is a decision between these possible arrangements, the other is a determination of the parameter v. Reflections in different orders from the basal plane (00·1), will be the same for the three structures and thus are best adapted to an estimation of v. The abnormally strong sixth order from this plane indicates that v is near to 5/8. This variable parameter does not enter into the intensity expressions of planes for which l = 0; consequently their reflections are the ideal ones for deciding between arrangements [e], [f] and [g]. Spectrometer measurements from the first three orders of (10·0) show better agreement with structure [e] though it is uncertain how conclusive would be a decision between [e] and [f] on the basis of this single observation.

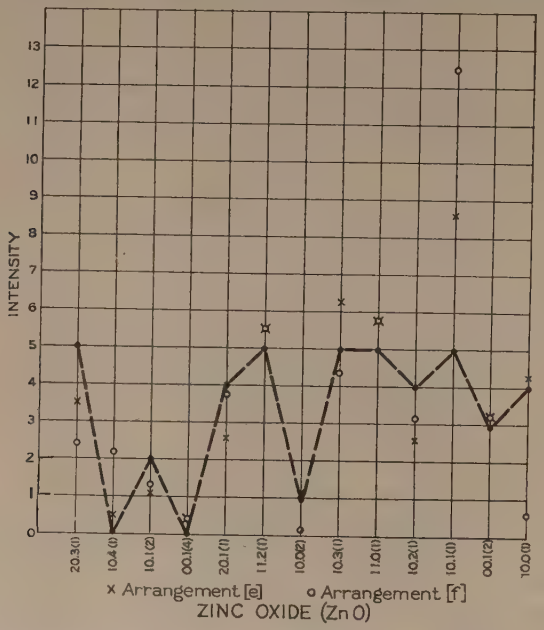


FIG. 168.—Points showing the observed relative intensities (*1922*, 5) of the principal lines from zinc oxide (ZnO) are connected by dashed lines. The calculated intensities of these lines for possible arrangements [e] and [f] are plotted as crosses and as open circles.

The Laue data are said to be explained almost equally well by [e] and [f]. The relative intensities of the first three lines in a powder photograph (*1922*, 5) of zincite and the absence of 10·4(1) conflict with the requirements of arrangement [f] (Figure 168). The intensities of the first few lines of another and better photograph (*1922*, 95) are shown in Figure 169. Except for greater intensities of 00·1(4) and 10·4(1) in these later

measurements, the two sets of data agree well with one another. The calculated intensities of Figure 168 were obtained by using $(d/n)^2$ for

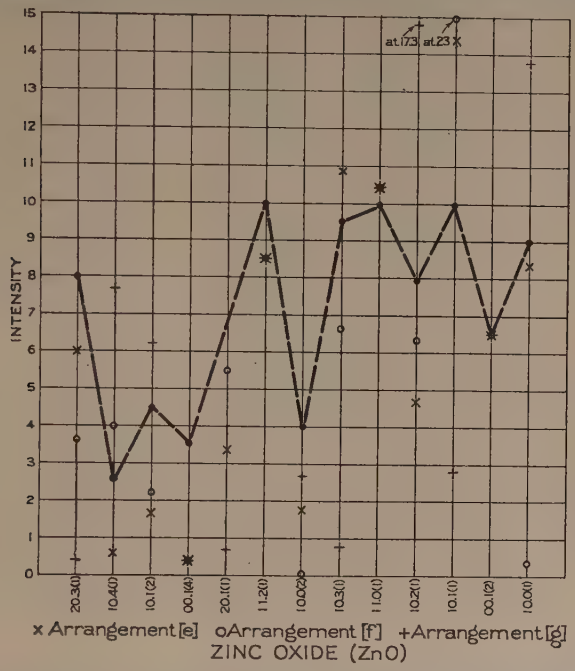


FIG. 169.—The dashed lines connect points giving the observed intensities (*1922*, 95) of the principal powder reflections of zinc oxide. The calculated intensities for the three possible structures [e], [f] and [g] are plotted as crosses, open circles and pluses. The ordinates are on twice the scale used in the preceding figure.

$f(d/n)$ in the equivalent of expression (26); for the intensities of Figure 169 $f(d/n)$ was taken proportional to $\frac{1 + \cos^2 2\theta}{2 \cos \theta \sin^2 \theta}$. The data of the second figure immediately eliminate [g] as a possible structure for ZnO; at the same time they confirm the results of Figure 168 in the conclusion that if the symmetry of zincite is that of 6e and if the chosen unit cell is not only the simplest one which fits these data but is actually the correct one, then the structure of ZnO is probably [e]. The intensities of other lines in these photographs do not conflict with this structure. Its structure factor, $A^2 + B^2$, is not sensitive to small changes in v and as a consequence the positions of the oxygen atoms cannot be more precisely established from the available data. The unit cell of [e] is shown in Figure 170; its dimensions are $a_0 = 3.251$A°, $c_0 = 5.226$A° (*1922*, 95).

Beryllium Oxide, BeO.—Crystals of BeO are known to have hexagonal symmetry. Powder photographs (*1922*, 59) which have the same general

characteristics as those of zincite make it highly probable that the two crystals have the same type of atomic arrangement—presumably [e] of

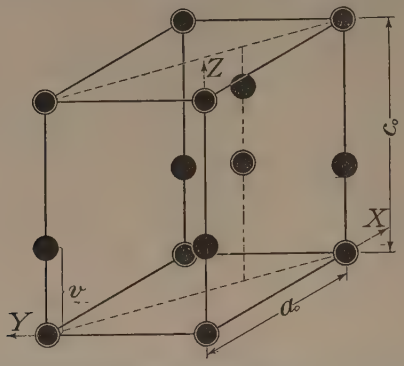


FIG. 170.—The unit cell of the zinc oxide arrangement [e']. According to the description in the text the zinc atoms are represented by ringed circles, the atoms of oxygen by full circles.

Figure 170. The sequences of relative intensities are similar, though of course not the same, in the two kinds of photographs.

From the powder photograph $a_0 = 2.696A°$ and $c_0 = 4.394A°$, corresponding to an axial ratio of $a : c = 1 : 1.63$. The parameter v defining the position of the oxygen atoms is perhaps near to 5/8, though it has not been established from these data.

An earlier powder investigation (*1922*, 36) of BeO was thought to establish a cubic sodium chloride arrangement of its atoms. It can be shown (*1922*, 59), however, that considering the resolution of these photographs all of the apparently cubic lines can be accounted for in terms of the hexagonal structure just described.

Calcium Oxide, CaO (1920, 19; 1921, 46; 1922, 36; 1923, 33a).—Crystals of CaO, like those of MgO, are optically isotropic and therefore have cubic symmetry. Powder photographs from CaO are similar to those from

TABLE V. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS OF CaO.

($\overline{N}_{Ca} = 18$, $\overline{N}_O = 10$)

INDICES		INTENSITY	
	Observed	Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	medium-strong	1.5	10
100(2)	strong	10	0.8
110(2)	strong	8.8	8.8
113(1)	medium-weak	1	6.5
111(2)	medium-weak	3.6	0.3
100(4)	weak	2	1.9
133(1)	weak	0.5	3.3
120(2)	strong	6	0.5
112(2)	medium-strong	4.9	4.8

MgO. From them the ratio m/n^3 is found to equal four. Except for an apparently too intense 111(1) reflection, the data of Table V show satisfactory intensity agreements with the demands of the sodium chloride arrangement [4b, 4c]. Lengths of the edge of the unit cube containing four molecules (Figure 167) have been given as 4.74A°, 4.77 ± 0.05A° (*1922*, 36), 4.84A° and 4.790 ± 0.004A° (*1923*, 33a).

Strontium Oxide, SrO (*1921, 46; 1922, 36*).—Strontium oxide is cubic and apparently isomorphous with CaO. Recorded lines in its powder photographs agree in position with those of a sodium chloride arrangement [4b, 4c] for which $a_0 = 5.104 \pm 0.01$A°. Their intensities do not give a thoroughly satisfactory fit with the requirements of this structure (Table VI). Strontium oxide takes up water and carbon dioxide with

TABLE VI. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS OF SrO

($\overline{N}_{Sr} = 36$, $\overline{N}_O = 10$)

INDICES	Observed	INTENSITY Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	very weak	5.9	10
100(2)	strong	10	2.6
110(2)	strong	8.8	7.2
113(1)	strong	3.9	6.5
111(2)	medium-weak	3.6	0.9
100(4)	medium-weak	1.9	1.6
133(1)	medium-weak	2	3.3
120(2)	medium-strong	6	1.6
112(2)	medium-strong	4.9	4.0

great readiness and it is very probable that these intensity disagreements are to be ascribed to a coincidence of impurity lines with those of the anhydrous oxide. Though it is likely that SrO has a sodium chloride arrangement of its atoms (Figure 167), more work is needed to correct these intensity irregularities.

Powder photographs[1] of a fusion of equal parts of CaO and SrO showed the principal powder lines of the sodium chloride arrangement with a value for a_0 midway between those for CaO and SrO. It thus appears that these oxides form solid solutions which remain stable down to room temperatures.

Barium Oxide, BaO (*1921, 46; 1922, 36*).—Barium oxide is cubic and presumably isomorphous with the other alkaline earth oxides. The published powder diffractions have the positions demanded by a sodium chloride arrangement [4b, 4c] (Figure 167) for which $a_0 = 5.50 \pm 0.02$A° or 5.47A°. The fact that the intensity data are in good agreement with this structure (Table VII) suggests that a better photograph from a less altered sample was obtained from BaO than from the analogous SrO.

[1] These photographs were made by the writer upon material furnished by P. Eskola. No data have yet been published.

TABLE VII. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS OF BaO ($\overline{N}_{Ba} = 54$, $\overline{N}_O = 10$)

INDICES	Observed	INTENSITY Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	medium-strong	8.8	10
100(2)	strong	10	3.4
110(2)	strong	8.9	6.4
113(1)	strong	5.7	6.5
111(2)	medium-strong	3.7	1.3
100(4)	medium-weak	2	1.4
133(1)	strong	3	3.3
120(2)	medium-strong	6	2.1
112(2)	medium-strong	4.9	3.6

Cadmium Oxide, CdO.—Optical examination shows that cadmium oxide, unlike zinc oxide, has cubic symmetry. Powder photographs (*1922*, 83) prove that $m/n^3 = 4$ and agree both in the positions and the intensities (Table VIII) of their lines with a sodium chloride arrangement [4b, 4c].

TABLE VIII. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS OF CdO ($\overline{N}_{Cd} = 46$, $\overline{N}_O = 10$)

INDICES	Observed	INTENSITY Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	medium-strong	7.7	10
100(2)	strong	10	3.1
110(2)	strong	8.9	7.0
113(1)	strong	5.0	6.5
111(2)	medium	3.6	1.2
100(4)	medium-weak	2	1.5
133(1)	medium	2.6	3.3
120(2)	strong	6	2.0
112(2)	strong	4.9	3.9

The length of the edge of the unit cube (Figure 167) is determined as $a_0 = 4.72$A° (*1920*, 19; *1922*, 83).

Nickel Oxide, NiO (*1920, 19; 1921, 28*).—It has been stated, without as yet the publication of any data, that NiO shows a sodium chloride arrangement [4b, 4c] of its atoms. The length of the edge of the unit cube (Figure 167) is given as $a_0 = 4.14$A° and 4.20A°. Uninterpreted measurements of a powder photograph have also appeared (*1922*, 43).

Cobalt Oxide, CoO (*1922, 43*).—Cobaltous oxide gives a powder photograph which has the general appearance of one arising from a sodium chloride arrangement. No determination of structure based upon data from this or other photographs has ever been made.

Dioxides.—As thorough as possible a study of structures has been carried out on the cubic, and isomorphous, dioxides of cerium, thorium and uranium. Satisfactory investigations of other dioxides have not yet been made. Nevertheless powder photographs and spectrometer measurements have been made upon quartz and spectrometer observations are

recorded upon the two tetragonal forms of TiO_2 and upon SnO_2, $ZrSiO_4$ and $ThSiO_4$.

Uranium Dioxide, UO_2 (1923, 41).—The crystals of natural UO_2, bröggerite, are optically isotropic. Laue photographs have been taken through sections of a crystal of bröggerite cut roughly parallel to (111) and (100) faces. These photographs show the appropriate symmetry characteristics but the crystals are not sufficiently perfect to yield results of great use in crystal structure determination. It is therefore necessary to rely upon the powder photographs which have been prepared from both powdered bröggerite and artificial UO_2. The usual interpretation of these photographs, which are essentially alike, combined with the density of UO_2 shows that $m/n^3 = 4$. No lines are found that require m to be greater than four. With the exception of a few faint lines which are in part not of constant occurrence and are probably due to impurities, all observed powder reflections are those to be expected from a face centered arrangement [4b] of atoms. The intensities of these lines are also approximately those given by such a grouping. In view of the overwhelmingly great scattering power of uranium compared with oxygen atoms, this must mean that the former have a face centered arrangement. Proceeding from this fact an inspection of the results of the theory of space groups (*1922*, 111) shows three possible arrangements with four molecules of UO_2 in the unit cube. They are:

[4b, 8e] Uranium atoms: $000;\ \frac{1}{2}\frac{1}{2}0;\ \frac{1}{2}0\frac{1}{2};\ 0\frac{1}{2}\frac{1}{2},$
Oxygen atoms: $\frac{111}{444};\ \frac{133}{444};\ \frac{313}{444};\ \frac{331}{444};\ \frac{333}{444};\ \frac{311}{444};\ \frac{131}{444};\ \frac{113}{444}.$

This, the calcium fluoride arrangement (Figure 171), can be deduced from the space groups Ti−3, O−3 and Oi−5.

[4d, 8d] Uranium atoms: $\frac{111}{444};\ \frac{133}{444};\ \frac{313}{444};\ \frac{331}{444},$
Oxygen atoms: $uuu;\ u\bar{u}\bar{u};\ \bar{u}u\bar{u};\ \bar{u}\bar{u}u;$

$u + \frac{1}{2}, u + \frac{1}{2}, \frac{1}{2} - u;\ \frac{1}{2} - u, \frac{1}{2} - u, \frac{1}{2} - u;\ u + \frac{1}{2}, \frac{1}{2} - u, u + \frac{1}{2};\ \frac{1}{2} - u, u + \frac{1}{2}, u + \frac{1}{2}.$

This arrangement can be obtained from the space groups Ti−2, O−2 and Oi−4.

[4b, 8h] Uranium atoms: $000;\ \frac{1}{2}\frac{1}{2}0;\ \frac{1}{2}0\frac{1}{2};\ 0\frac{1}{2}\frac{1}{2},$

Oxygen atoms: $uuu;\ u + \frac{1}{2}, \frac{1}{2} - u, \bar{u};\ \bar{u}, u + \frac{1}{2}, \frac{1}{2} - u;\ \frac{1}{2} - u, \bar{u}, u + \frac{1}{2};\ \bar{u}\bar{u}\bar{u};\ \frac{1}{2} - u, u + \frac{1}{2}, u;\ u, \frac{1}{2} - u, u + \frac{1}{2};\ u + \frac{1}{2}, u, \frac{1}{2} - u.$

This, the pyrite arrangement (Figure 176) arises from the space group Ti−6.

Neither crystals of UO_2 nor those of the isomorphous thorium and cerium dioxides show any evidence of pyritohedral symmetry. For this reason [4b, 8h] is somewhat improbable as the correct atomic arrangement. Because of the insignificant effect of the oxygen atoms it is, however, not possible either to eliminate definitely this structure or to make any

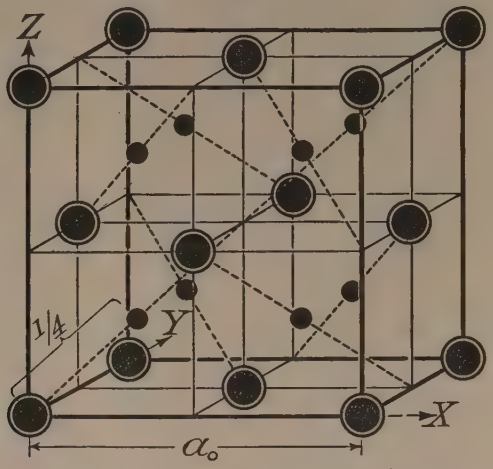


FIG. 171.—The unit cube of the "calcium fluoride arrangement" [4b, 8e]. Calcium atoms, [4b], are represented by ringed circles, the fluorine atoms, [8e], by small black circles.

final choice between these three arrangements. Of the first two the calcium fluoride structure has that degree of probability which attaches to the fact that it, but not [4d, 8d] has been found for other crystals.

The powder data upon both bröggerite and artificial UO_2 lead to 5.47A° as the length of the edge of the unit cube containing four molecules.

Thorium Dioxide, ThO_2 (1923, 41).—Thorium dioxide gives the same type of powder photograph as UO_2. It thus presumably contains four chemical molecules within the unit cell and has its thorium atoms arranged according to the face centered cubic arrangement [4b]. The length of the edge of this unit was found to be $a_0 = 5.61$A°. As was true of UO_2 several faint lines were observed besides those to be expected from the thorium atoms alone or from a calcium fluoride arrangement for ThO_2; although indices can be assigned to these lines it seems more probable that they are due to impurities.

Thorianite (Th, U)O_2 (1923, 41).—A powder photograph from a sample of Ceylon thorianite was similar to the photographs from UO_2 and ThO_2. The length of the side of the unit cell containing four molecules was found to be $a_0 = 5.57$A°. Material from this same locality (the Galle district)

has been found to contain from 27–33% of UO_2 and from 1–2% of the rare earths.

Cerium Dioxide, CeO_2 (1923, 41).—Cerium dioxide gives a pattern similar to that of the other two oxides. It was grown in crystals of microscopic size and showed itself to be optically isotropic. As the calculations and intensity data of Table IX will show, the cerium atoms are light enough

TABLE IX. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS OF CeO_2 ($\overline{N}_{Ce^{++++}} = 54$, $\overline{N}_{O''} = 10$)

INDICES	Observed	INTENSITY Calc. for Ce atoms alone	Calc. for [4b, 8e]
111(1)	very strong	10	10
100(2)	weak	5.4	2.1
110(2)	very strong	4.7	8.9
113(1)	very strong	6.5	6.5
111(2)	very weak	1.9	0.8
100(4)	weak	1.0	2.0
133(1)	strong	3.3	3.3
120(2)	medium [1]	3.2	1.3
112(2)	very strong	2.6	4.9

so that the presence of oxygen has become definitely appreciable. It is therefore worth while to compare the intensity requirements of the most probable structure—the calcium fluoride arrangement [4b, 8e]—with the observed intensities of the powder lines.

The A and B terms in the structure factor of expression (26) for [4b, 8e] have the following values:

$$\left.\begin{array}{l}
\text{When n is odd:} \\
\quad \text{If the indices are two odd and one even or two even and one odd, } A = B = 0; \\
\quad \text{If the indices are all odd, } A = 4\overline{Ce},\ B = 0; \\
\text{When n = 2, 6, etc.:} \\
\quad \text{If the indices are two even and one odd or all odd, } A = 4\overline{Ce} - 8\overline{O},\ B = 0; \\
\quad \text{If the indices are two odd and one even, } A = 4\overline{Ce} + 8\overline{O},\ B = 0; \\
\text{When n = 4, 8, etc.:} \\
\quad A = 4\overline{Ce} + 8\overline{O},\ B = 0 \text{ always.}
\end{array}\right\} \quad (38)$$

An application of these quantities in (26) leads to the intensities of the fourth column of Table IX. Their good agreement with the observed intensities makes it increasingly probable that crystals of CeO_2 (and by

[1] This line is particularly strong in the photographs because the unscreened K-β reflection from 211(2) is contributing to it.

inference those of ThO_2 and UO_2) have this calcium fluoride arrangement of their atoms (Figure 171). A few faint lines were found which must be attributed to impurities if CeO_2 has this atomic grouping. Since a small amount of foreign material was known to be present, the occurrence of such doubtful lines is not surprising.

The length of the edge of the unit cube containing four molecules was determined to be $a_0 = 5.41A°$.

Quartz, SiO_2.—The low temperature form of quartz is the only crystalline modification of silica for which an attempt at crystal structure determination has been made. Laue photographs (*1915*, 18; *1916*, 15) have been produced but only data from spectrometric (*1914*, 4) and powder photographic measurements (*1923*, 67) have been used in assigning atomic arrangements. None of the treatments of these observations are adequate for establishing the probably correct atomic grouping. Two structures have been suggested upon the basis of the spectrometer reflections; one is purely hexagonal (*1914*, 4), in the other the silicon atoms lie upon a rhombohedral lattice (*1920*, 2). An arrangement has also been suggested (*1923*, 67) which is said to be in qualitative agreement with the powder data from quartz; these data have not, however, yet been published.

Rutile, TiO_2.—Two spectrometric studies have been made upon crystals of rutile. The experimental results are not the same and as a consequence the suggested arrangements are different. One of these seems almost too complicated to be correct (*1917*, 27); the other (*1916*, 31) may be a probably correct structure but the existing data and their treatment are insufficient to prove it.

Anatase, TiO_2 (1916, 32) and Zircon, $ZrSiO_4$ (1916, 31).—Spectrometer observations have been made upon each of these tetragonal crystals. The data and their treatment do not seem capable of establishing their atomic arrangements.

Cassiterite, SnO_2.—The experimental data (*1916*, 31; *1917*, 27) and their treatment for stannic oxide are similar to but less complete than those for rutile. Unanalyzed powder data (*1922*, 43) and Laue photographs (*1916*, 14) have been published. It has also been shown (*1923*, 103) that stannic oxides precipitated under various conditions all give the same diffraction pattern as macro-crystalline SnO_2. Both the alpha- and the meta-stannic acids are composed of minute crystals of SnO_2: the crystals of the alpha-form are smaller than those of the other.[1]

Thorite, $ThSiO_4$ (1916, 31).—Crystals of thorite, which is commonly related crystallographically to the preceding tetragonal minerals, did not give spectrometer reflections. This is not surprising in view of the fact that thorite is ordinarily found in an altered condition.

[1] From unpublished data of E. W. Posnjak.

Trioxides

Alumina, Al_2O_3 and Hematite, Fe_2O_3.—A few spectrometer observations (*1915*, 4, p. 169) have been made upon Al_2O_3 and Fe_2O_3. From them a structure has been proposed which resembles that of calcite. These data and their treatment are not, however, adequate for determinations of atomic arrangement. Powder photographs (*1922*, 43) have been prepared from Al_2O_3 made under different conditions; but no attempt was made to analyze them. The effect of temperature (*1922*, 7) upon the intensities and positions of diffraction effects has been illustrated through some spectrometer reflections obtained at temperatures up to 950°C. The change in relative atomic positions within the crystal which accompanies this heating is shown by the more rapid decrease of the intensity of 111(1) than of 111(2) with increase in temperature.

Arsenic Trioxide, As_2O_3 (1923, 15).—Arsenic trioxide is dimorphous. The form stable at low temperatures crystallizes in octahedrons and is commonly supposed to have cubic symmetry. Its crystals, however, exhibit optical anomalies which have sometimes been held to prove that the true symmetry is pseudo-cubic rather than cubic.

Proceeding upon the assumption that their symmetry really is cubic the following study has been made of the structure of crystals of As_2O_3. Octahedral crystals were prepared by cooling a hydrochloric acid solution of As_2O_3 containing small quantities of sodium chloride. Reflection spectrum photographs from the (100), (110) and (111) faces of these crystals show that the smallest unit consistent with them has a length of edge of $a_0 = 11.06A°$. This knowledge combined with the known density yields $m/n^3 = 16$. There is no evidence either from these spectrographic measurements or from the Laue photographs to indicate that m should be greater than 16. The reflections from single faces further show that up through the eighth order of reflection, only fourth and eighth order spectra are to be found from (100), that odd orders are absent from the (110) face and that all orders of reflection are present from (111). In accord with these observations are the Laue photographic data which give first order reflections only from planes with all odd indices and second order spots both from planes with two even and one odd and with two odd and one even indices. Furthermore reflections are missing from the only two planes (0kl), where k and l are one even and the other odd, which were in positions to give second order effects. These data suggest (see page 219) that the corresponding space group for this crystal is Oi − 7. If it is assumed that the arsenic atoms are alike and that the oxygen atoms are also alike, then a consideration of all of the special cases of the cubic space groups shows that this assignment to Oi − 7 is the only one possible and that the

atomic positions of the arsenic atoms are given by the coördinates (*1922*, 111):

(32b) uuu; $u+\frac{1}{2}, u+\frac{1}{2}, u$; $u+\frac{1}{2}, u, u+\frac{1}{2}$; $u, u+\frac{1}{2}, u+\frac{1}{2}$;
$u\bar{u}\bar{u}$; $u+\frac{1}{2}, \frac{1}{2}-u, \bar{u}$; $u+\frac{1}{2}, \bar{u}, \frac{1}{2}-u$; $u, \frac{1}{2}-u, \frac{1}{2}-u$;
$\bar{u}u\bar{u}$; $\frac{1}{2}-u, u+\frac{1}{2}, \bar{u}$; $\frac{1}{2}-u, u, \frac{1}{2}-u$; $\bar{u}, u+\frac{1}{2}, \frac{1}{2}-u$;
$\bar{u}\bar{u}u$; $\frac{1}{2}-u, \frac{1}{2}-u, u$; $\frac{1}{2}-u, \bar{u}, u+\frac{1}{2}$; $\bar{u}, \frac{1}{2}-u, u+\frac{1}{2}$;
$\frac{1}{4}-u, \frac{1}{4}-u, \frac{1}{4}-u$; $\frac{3}{4}-u, \frac{3}{4}-u, \frac{1}{4}-u$; $\frac{3}{4}-u, \frac{1}{4}-u, \frac{3}{4}-u$; $\frac{1}{4}-u, \frac{3}{4}-u, \frac{3}{4}-u$;
$\frac{1}{4}-u, u+\frac{1}{4}, u+\frac{1}{4}$; $\frac{3}{4}-u, u+\frac{3}{4}, u+\frac{1}{4}$; $\frac{3}{4}-u, u+\frac{1}{4}, u+\frac{3}{4}$; $\frac{1}{4}-u, u+\frac{3}{4}, u+\frac{3}{4}$;
$u+\frac{1}{4}, \frac{1}{4}-u, u+\frac{1}{4}$; $u+\frac{3}{4}, \frac{3}{4}-u, u+\frac{1}{4}$; $u+\frac{3}{4}, \frac{1}{4}-u, u+\frac{3}{4}$; $u+\frac{1}{4}, u+\frac{3}{4}, \frac{3}{4}-u$;
$u+\frac{1}{4}, u+\frac{1}{4}, \frac{1}{4}-u$; $u+\frac{3}{4}, u+\frac{3}{4}, \frac{1}{4}-u$; $u+\frac{3}{4}, u+\frac{1}{4}, \frac{3}{4}-u$; $u+\frac{1}{4}, u+\frac{3}{4}, \frac{3}{4}-u$.

The coördinates of the oxygen atoms similarly must be:

(48c) $v00$; $v+\frac{1}{2}, \frac{1}{2}, 0$; $v+\frac{1}{2}, 0, \frac{1}{2}$; $v\frac{1}{2}\frac{1}{2}$;
$\bar{v}00$; $\frac{1}{2}-v, \frac{1}{2}, 0$; $\frac{1}{2}-v, 0, \frac{1}{2}$; $\bar{v}\frac{1}{2}\frac{1}{2}$;
$0v0$; $\frac{1}{2}, v+\frac{1}{2}, 0$; $0, v+\frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}v\frac{1}{2}$;
$0\bar{v}0$; $\frac{1}{2}, \frac{1}{2}-v, 0$; $0, \frac{1}{2}-v, \frac{1}{2}$; $\frac{1}{2}\bar{v}\frac{1}{2}$;
$00v$; $\frac{1}{2}, 0, v+\frac{1}{2}$; $0, \frac{1}{2}, v+\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}v$;
$00\bar{v}$; $\frac{1}{2}, 0, \frac{1}{2}-v$; $0, \frac{1}{2}, \frac{1}{2}-v$; $\frac{1}{2}\frac{1}{2}\bar{v}$;
$\frac{1}{4}-v, \frac{1}{4}, \frac{1}{4}$; $\frac{3}{4}-v, \frac{3}{4}, \frac{1}{4}$; $\frac{3}{4}-v, \frac{1}{4}, \frac{3}{4}$; $\frac{1}{4}-v, \frac{3}{4}, \frac{3}{4}$;
$v+\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; $v+\frac{3}{4}, \frac{3}{4}, \frac{1}{4}$; $v+\frac{3}{4}, \frac{1}{4}, \frac{3}{4}$; $v+\frac{1}{4}, \frac{3}{4}, \frac{3}{4}$;
$\frac{1}{4}, \frac{1}{4}-v, \frac{1}{4}$; $\frac{3}{4}, \frac{3}{4}-v, \frac{1}{4}$; $\frac{3}{4}, \frac{1}{4}-v, \frac{3}{4}$; $\frac{1}{4}, \frac{3}{4}-v, \frac{3}{4}$;
$\frac{1}{4}, v+\frac{1}{4}, \frac{1}{4}$; $\frac{3}{4}, v+\frac{3}{4}, \frac{1}{4}$; $\frac{3}{4}, v+\frac{1}{4}, \frac{3}{4}$; $\frac{1}{4}, v+\frac{3}{4}, \frac{3}{4}$;
$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}-v$; $\frac{3}{4}, \frac{3}{4}, \frac{1}{4}-v$; $\frac{3}{4}, \frac{1}{4}, \frac{3}{4}-v$; $\frac{1}{4}, \frac{3}{4}, \frac{3}{4}-v$;
$\frac{1}{4}, \frac{1}{4}, v+\frac{1}{4}$; $\frac{3}{4}, \frac{3}{4}, v+\frac{1}{4}$; $\frac{3}{4}, \frac{1}{4}, v+\frac{3}{4}$; $\frac{1}{4}, \frac{3}{4}, v+\frac{3}{4}$.

By making only the most qualitative use of the two "laws" of scattering, it can be shown with expression (20) that the relative intensities of the Laue spots can be accounted for only when $u = 0.895 \pm 0.005$ and $v = \pm 0.21$.

The arrangement [32b, 48c] of the atoms in cubic crystals of As_2O_3 as determined in this manner is shown in Figure 172. This structure is most simply interpreted as a diamond arrangement of As_4O_6 molecules; in this grouping half of the molecules (the ones occupying positions analogous to those of the zinc atoms in cubic zinc sulfide) have one orientation, the other half (corresponding to the sulfur atoms in ZnS) are differently turned with respect to the coördinate axes. Within each of these molecules every arsenic atom is nearest to three oxygen atoms and each oxygen atom

is equidistant from two arsenic atoms; there is thus no necessary conflict between this structure and the demands of the old rules of valence.

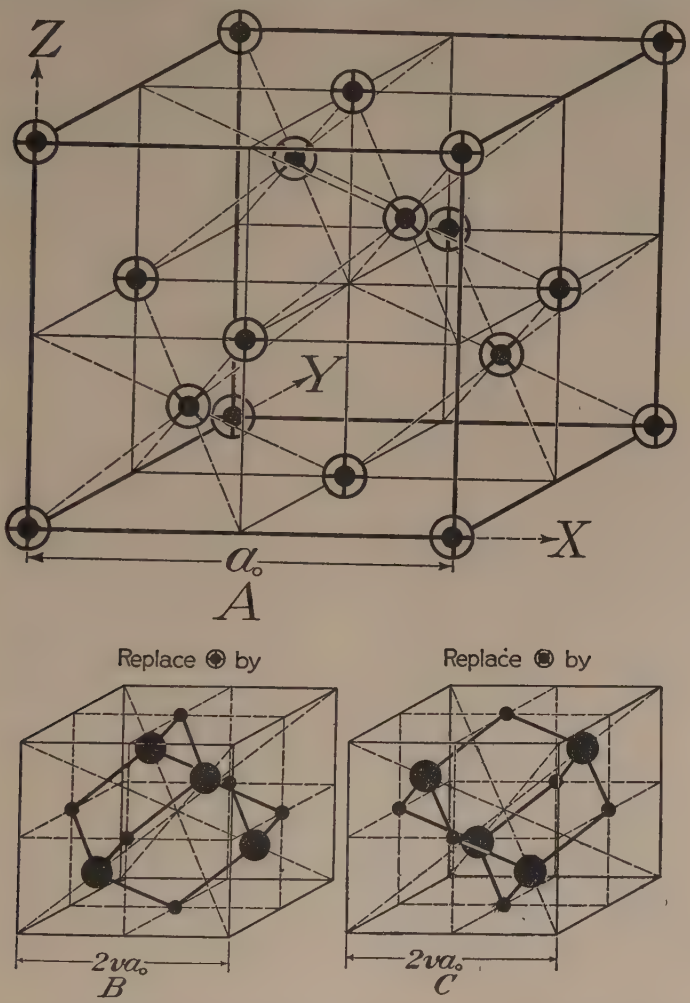


FIG. 172.—The unit cube of the atomic arrangement in cubic As_2O_3. For the reconstruction of this atomic grouping the symbols ⊕ and ⊛ in A should be replaced by B and C; the centers of the symbols are to be taken coincident with the centers of the small cubes. Large black circles represent the arsenic atoms; the small circles are atoms of oxygen.

Antimonous Oxide, Sb_2O_3 (1923, 15).—Crystals of Sb_2O_3 are obtained which are crystallographically isomorphous with the cubic modification of As_2O_3; they present the same sort of optical anomalies which have been

mentioned for As_2O_3. Assuming that their symmetry is truly cubic, the atomic arrangement in crystals of Sb_2O_3, as the mineral senarmontite, was determined by the same process followed in studying arsenic trioxide. The crystal used contained about 3% of arsenic, a trace of bismuth and about 10% of alkaline earths (presumably in mechanical admixture).

The diffraction data, from spectrographic measurements and Laue photographs, are strictly analogous to those from As_2O_3 and lead to the same type of atomic arrangement. The calculated structure factors agree qualitatively with the intensities of the observed reflections when $u = 0.885 \pm 0.005$ and $v = \pm 0.23$.

The length of the edge of the unit cube containing eight molecules of Sb_4O_6 (Figure 172) was found to be $a_0 = 11.14A°$.

Uranium Trioxide, UO_3 (1923, 41).—Powder photographs have been made from UO_3 prepared by heating ammonium uranate for 16 hours at 230°C and then for 20 hours at 160°–270°C. Aside from a few faint lines which can be attributed to U_3O_8, these photographs showed only a general blackening. It thus appears that UO_3 made in this way is completely amorphous.

Cleveite (1923, 41).—Powder photographs of this mineral from three different localities have been examined. Material from two of these sources has been analyzed and found to be predominantly UO_3 in composition. Nevertheless all of the powder patterns consisted of the lines of UO_2 on blackened backgrounds. The dimensions of the unit cubes also proved to be identical with those of pure UO_2, namely $a_0 = 5.47A°$. In order to shed more light upon the problem of this identity in pattern with UO_2, cleveite was heated for one half hour at 800°C; at the conclusion of this treatment the powder pattern was predominantly that of U_3O_8 and very faintly that of UO_2. Bröggerite (UO_2) heated under these same conditions continued to give only the pattern of UO_2. From these observations it is thought possible that cleveite consists of a UO_2 structure which has dissolved oxygen; the data do not, however, appear to preclude the possibility of it being composed of amorphous UO_3 with an admixture of a comparatively small proportion of as yet unaltered UO_2.

Other Oxides

Pitchblende (1923, 41).—Powder photographs have been obtained from two specimens of pitchblende. That from Joachimstal showed strongly but upon a blackened field the same planar reflections that have been observed in UO_2. The other sample (locality unknown) gave the strongest of these lines. In both photographs there was an appreciable broadening of the reflections which points to a minuteness in the size of the individual crystals. From these photographs it appears probable that pitchblende

consists of a mixture of some crystalline UO_2 with amorphous and more or less oxidized and altered higher oxides of uranium. The slightly smaller spacings of UO_2 ($a_0 = 5.42 - 5.45$A°) in this mineral are probably to be ascribed to the presence of lead and other metals in solid solution.

U_3O_8 (1923, 41).—This oxide was prepared by heating UO_3 in air. A specimen which had been heated at ± 785°C for 37 hours gave a powder photograph in which the lines were broadened due to the minute size of the individual crystals. Another preparation made by heating UO_3 at ± 1040°C for eight hours was crystalline under the microscope and yielded a powder photograph of sharp lines. The observed lines in these patterns are not those of a cubic crystal; this fact agrees with the apparent double refraction of the crystals in the preparation grown at ± 1040°C. No attempt has been made to deduce either their symmetry or their structure from the powder data.

Hydroxides

The isomorphous magnesium and manganous hydroxides are the only hydroxides for which attempts have been made to determine atomic arrangement.

Pyrochroite, $Mn(OH)_2$ (1919, 2).—Laue photographs alone are available for this crystal which is ordinarily assigned the symmetry of the holohedral class of the rhombohedral division of the hexagonal system, 3Di. A photograph taken with the X-rays normal to the base, (00·1), showed trigonal with a close approach to hexagonal symmetry. Most of the observed spots did not fulfill the demands of the criterion which has been suggested to distinguish the rhombohedral from the hexagonal lattice; the unit cell has consequently been assumed to be an hexagonal prism. Calculations of wave lengths of reflection together with a knowledge of the shortest wave lengths present in the primary beam show that a unit having the following dimensions agrees with the data: $a_0 = 3.34$A°, $c_0 = 4.68$A°, corresponding to the axial ratio $a : c = 1 : 1.40$. From the density it is found that one molecule of $Mn(OH)_2$ is contained within this cell.

If it is assumed that the crystallographically determined symmetry class, 3Di, represents the symmetry of atomic arrangement, then a reference to the results of the theory of space groups shows that the following arrangement is the only one possible for the single molecule unit (see 3Di−3):

[h] Manganese atom: 000,
Oxygen atoms: $\frac{1}{3}\ \frac{2}{3}\ u$; $\frac{2}{3}\ \frac{1}{3}\ \bar{u}$,
Hydrogen atoms: presumably the same as oxygen with a different value for u.

By plotting the values of the structure factor for different values of u for such pairs of forms as 05·2 and 50·2, it can be shown without any quantitative use of the "laws" of scattering that

$$0.166 < u < 0.25.$$

After calculating the relative intensities of the different Laue spots using as good scattering assumptions as are available, it is thought that u = 0.22 = 2/9 furnishes the most satisfactory agreement within this range.

The unit cell of this structure for $Mn(OH)_2$ is shown in Figure 173.

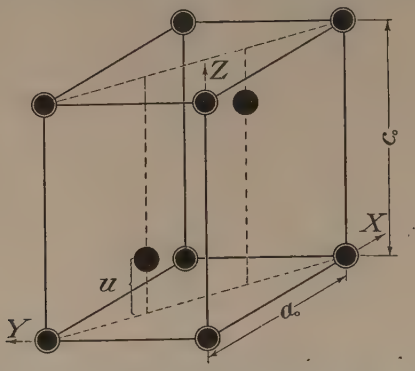


FIG. 173.—The unit cell of the pyrochroite arrangement [h]. The manganese atoms are designated by ringed circles, the oxygen atoms by black circles. No positions are shown for the hydrogen atoms.

It should be noted that the dimensions—$a_0 = 3.34A°$, $c_0 = 4.68A°$—have not been obtained by accurate diffraction measurements.

Brucite, $Mg(OH)_2$.—Laue photographs (*1919*, 2) of two specimens of manganese-bearing brucites were found to be similar to those from pyrochroite and led to the atomic arrangement that has just been described for $Mn(OH)_2$. As well as could be determined the parameter u defining the positions of the oxygen atoms is the same as in pyrochroite. A powder photograph (*1921*, 3) of precipitated pure $Mg(OH)_2$ gave data in accord with this assignment of structure but it could not be used for a more accurate placing of the oxygen atoms. The dimensions of the unit cell (Figure 173) were not deduced from this photograph but its results are in approximate agreement with the calculated dimensions for $Mg(OH)_2$: $a_0 = 3.13A°$, $c_0 = 4.75A°$, corresponding to an axial ratio of a : c = 1 : 1.521.

Sulfides, Selenides, etc.

Monosulfides, etc., of the Univalent Metals

Cuprous Selenide, Cu_2Se (1923, 33b).—It is stated, without as yet the publication of any data, that Cu_2Se has cubic symmetry and crystallizes in

the calcium fluoride arrangement [4b, 8e] (Figure 171). The unit cell is given as: $a_0 = 5.751 \pm 0.007A°$.

Monosulfides, etc., of the Divalent Metals

Magnesium Sulfide, MgS (1923, 50).—Magnesium sulfide is supposed to crystallize in the cubic system. Its powder photograph gives lines which agree with this symmetry and show that $m/n^3 = 4$. There are no data to indicate that m should be greater than four. With the exception of one line, to which rational indices can be assigned but which more probably is due to impurities in the magnesium sulfide, all of the observed lines are those characteristic of [4b, 4c] and [4b, 4d], the sodium chloride and zinc sulfide arrangements. Taking the atomic scattering powers as proportional to the electron numbers of doubly charged magnesium and sulfur "ions," the calculated intensities for these two structures are compared with observation in Table X. It is immediately apparent that the

TABLE X. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM MgS ($\overline{N}_{Mg} = 10$; $\overline{N}_S = 18$)

INDICES	Observed	INTENSITY Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	absent	1.5	10
100(2)	very strong	10	0.8
110(2)	very strong	8.8	8.8
113(1)	weak	1.0	6.5
111(2)	very strong	3.6	0.3
100(4)	medium	2.0	1.9
133(1)	weak	0.5	3.3
120(2)	very strong	6.0	0.5
112(2)	very strong	4.9	4.8

zinc sulfide structure must be excluded; the agreement with the sodium chloride arrangement [4b, 4c], which these data then indicate as the correct one, is probably as good as the experimental estimates of intensity.

From these data the unit cube (Figure 167) is found to have a length of edge : $a_0 = 5.078 \pm 0.012A°$.

Calcium Sulfide, CaS (1923, 50).—Crystals of CaS have cubic symmetry. The powder pattern is analogous to that of MgO and leads to $m/n^3 = 4$ with no evidence for a value of m greater than four. Except for one line, which probably is to be ascribed to an impurity, the observed reflections indicate either a sodium chloride or a zinc sulfide arrangement. The comparison between the calculated intensities for these two arrangements and the observed intensities of diffraction lines (Table XI) eliminates [4b, 4d] and shows acceptable agreement with the sodium chloride structure [4b, 4c]. If, as seems probable, the calcium and sulfur atoms are

TABLE XI. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM CaS ($\bar{N}_{Ca} = 18$; $\bar{N}_S = 18$)

INDICES	Observed	INTENSITY Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	absent	0	10
100(2)	very strong	10	0
110(2)	very strong	8.9	9.5
113(1)	weak	0	6.5
111(2)	strong	3.7	0
100(4)	strong	2.0	2.1
133(1)	absent	0	3.3
120(2)	very strong	6.0	0
112(2)	very strong	4.9	5.2

charged, then there would be no odd order reflections from planes with all odd indices if the scattering powers were simply proportional to the electron number of atoms. Nevertheless though 111(1) was not observed, 113(1) and 133(1) were found. Such facts agree with the statement that this proportionality becomes less accurately fulfilled the less the spacings between identical reflecting planes.

These data (*1923*, 50) lead to a length of edge of the unit cube (Figure 167) of $a_0 = 5.600 \pm 0.008$A°. Another determination (*1923*, 33a), upon which no data have appeared, is said to yield $a_0 = 5.686 \pm 0.006$A°.

Strontium Sulfide, SrS (*1923*, *50*).—Strontium sulfide is supposed to give crystals with cubic symmetry. Its powder photograph fits this symmetry and shows that $m/n^3 = 4$, with no evidence for a value of m greater than four. The diffraction lines are those to be expected from the sodium chloride or the zinc sulfide arrangements. As the intensity calculations of Table XII show, the structure cannot be the latter. The agreement

TABLE XII. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM SrS ($\bar{N}_{Sr} = 36$; $\bar{N}_S = 18$)

INDICES	Observed	INTENSITY Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	absent	2.1	10.0
100(2)	very strong	10.0	1.1
110(2)	very strong	8.8	8.5
113(1)	medium	1.3	6.5
111(2)	strong	3.6	0.4
100(4)	strong	2.0	1.9
113(1)	medium	0.7	3.3
120(2)	very strong	6.0	0.6
112(2)	strong	4.9	4.7

with the requirements of the sodium chloride arrangement [4b, 4c] is fair and probably as good as the experimental estimates of intensity.

The length of the edge of the unit cube (Figure 167) as obtained from these data is $a_0 = 5.866 \pm 0.011$A°.

Barium Sulfide, BaS (1923, 50).—The powder pattern of BaS is strictly analogous to that of the other alkaline earth sulfides and meets the demands of a cubic crystal containing four molecules within the unit cell. As the intensity calculations of Table XIII indicate, the zinc sulfide arrangement

TABLE XIII. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM BaS ($\overline{N}_{Ba} = 54$; $\overline{N}_S = 18$)

INDICES	Observed	INTENSITY Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	weak	4.7	10.0
100(2)	very strong	10.0	2.1
110(2)	very strong	8.8	7.5
113(1)	strong	3.0	6.5
111(2)	medium	3.6	0.8
100(4)	strong	2.0	1.7
133(1)	medium	1.6	3.3
120(2)	very strong	6.0	1.3
112(2)	very strong	4.9	4.2

is an impossible one for this crystal. The structure is thus probably the sodium chloride grouping [4b, 4c] (Figure 167) though the intensity fit is not so good as usual. It seems probable that this is due partly to impurities in the BaS; better agreement might also result from a more accurate estimation of the intensities of the powder lines.

The length of the edge of the unit cell, as determined from these measurements, is $a_0 = 6.346 \pm 0.003$A°.

Zinc Blende, ZnS (1913, 6; 1914, 12, 18; 1922, 37).—Zinc blende is the cubic modification of ZnS. Its face development is that of a crystal having the symmetry of the point group Te. Spectrometric observations, Laue and powder photographs have all been prepared. The spectrometer measurements show that $m/n^3 = 4$ and point to the arrangement [4b, 4d] as the probable one. Neither the Laue nor the powder data suggest that m should be greater than four. The presence of only reflections with all odd indices in odd orders combined with the results of space group theory (see page 215) leads to either structure [4b, 4c] or structure [4b, 4d]. The ntensity data from any of these experiments, but best the powder data, show that the sodium chloride grouping is an impossible one; at the same time they yield (Table XIV) satisfactory agreement with the zinc sulfide grouping [4b, 4d].

The arrangement of the atoms in the cubic crystals of ZnS must then be the following (Figure 174):

[4b, 4d] Zinc atoms: 000; $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$,
Sulfur atoms: $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{3}{4}\frac{3}{4}\frac{1}{4}$; $\frac{3}{4}\frac{1}{4}\frac{3}{4}$; $\frac{1}{4}\frac{3}{4}\frac{3}{4}$.

TABLE XIV. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM ZINC BLENDE ($\overline{N}_{Zn} = 28$; $\overline{N}_S = 18$)

INDICES	INTENSITY		
	Observed	Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	4	0.9	10.0
100(2)	1	10.0	0.5
110(2)	4	8.8	9.0
113(1)	4	0.6	6.5
111(2)	1	3.6	0.2
100(4)	2	2.0	2.0
133(1)	3	0.3	3.3
120(2)	0	6.0	0.3
112(2)	4	4.9	5.0

The length of the edge of the unit cube deduced from the spectrometer measurements was $a_0 = 5.42$A°; from the powder data it was found to be $a_0 = 5.40$A° (*1922*, 37).

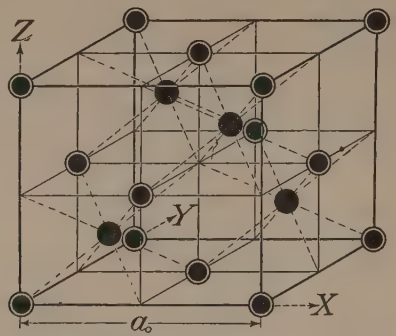


FIG. 174.—The unit cube of the zinc sulfide arrangement [4b, 4d]. Either the zinc or the sulfur atoms can be represented by the ringed circles.

Wurtzite, ZnS.—Wurtzite, the hexagonal modification of ZnS, is generally considered to be isomorphous with zincite, ZnO. The powder photograph (*1923*, 1) to which it gives rise has the same general characteristics as that from ZnO. Taking the unit cell for wurtzite to be the same as that for zincite, the absence of odd order powder reflections from planes for which $2h + k = 3p$ (see page 273) limits the possible structures to [e], [f] and [g], described under ZnO. Reflections having $l = 0$ are best suited for deciding between these possibilities because they are uninfluenced by the value of the variable parameter u. In Table XV the calculated intensities [using an expression analogous to (26) except that $(d/n)^2$ replaces $(d/n)^{2.35}$] for each of these three possible arrangements are compared with those obtained upon the powder photograph. They are obviously incapable of deciding definitely between [e] and [g]; neither are any other available data. Certain reflections appear

TABLE XV. INTENSITY DATA UPON POWDER REFLECTIONS FROM WURTZITE (ZnS) WHICH HAVE $l = 0$

INDICES	Observed	INTENSITY Calc. for [e]	Calc. for [f]	Calc. for [g]
10.0(1)	2	8.89 units	0.27 units	6.06 units
11.0(1)	4	8.67	8.67	8.67
10.0(2)	0	1.46	0.04	0.99
21.0(1)	1	1.57	0.05	1.07
10.0(3)	3	3.03	3.03	3.03

too strong for a zinc oxide structure [e]. Similar anomalously intense reflections have been observed from the structurally related silver iodide. Recent work (*1923*, 91) upon this latter substance with instruments of greater resolving power seems to prove that it usually consists of a mixture of cubic and hexagonal modifications; it may be that wurtzite actually has the zinc oxide structure and that apparent anomalies are to be attributed to a similar admixture of cubic crystals of ZnS. Whatever the correct explanation it is clear that additional experiments with spectrographs of greater resolving power are needed before a satisfactory atomic arrangement is established.

If the zinc oxide arrangement (Figure 170) is the correct one for wurtzite then the powder photographic data lead to a unit cell of the following dimensions: $a_0 = 3.80\text{A}°$, $c_0 = 6.23\text{A}°$, corresponding to the axial ratio $a : c = 1 : 1.638$.

A single basal reflection (*1920*, 11) from a crystal of wurtzite was also found to be compatible with a zincite, [e], grouping.

Greenockite, CdS (*1920, 11*).—Crystals of CdS have hexagonal symmetry. A single spectrometer measurement was found to be not inconsistent with a zinc oxide arrangement [e].

Mercury Sulfide, HgS.—Natural crystals of HgS are found in two modifications—a trigonal one, cinnabar; and a cubic one, metacinnabarite. The crystal structure of neither has been adequately determined. Some spectrometer measurements (*1923*, 64) have been made upon cinnabar; the structure suggested by them is built upon a unit containing three molecules. These data and their treatment are not, however, adequate for establishing the probable structure. No diffraction data of any sort have yet been published upon the presumably cubic metacinnabarite.

Galena, PbS.—It has been stated (*1915*, 4, p. 173), presumably on the basis of spectrometer observations, that the atoms of galena have the sodium chloride arrangement [4b, 4c]. No data, however, appear ever to have been published.

Alabandite, MnS (*1921, 95*).—Crystals of MnS are isotropic and therefore cubic in symmetry. Data from a comparison photograph from

the (100) faces of calcite and alabandite, combined with the density, lead to $m/n^3 = 4$. Some crystallographic observations have been thought to show that MnS is either tetartohedral or tetrahedral in symmetry. The lines of its powder photograph are only those to be expected from either the sodium chloride or the zinc sulfide arrangement. It must consequently be concluded that if MnS has less than holohedral symmetry due to the arrangement of its atoms, the grouping must be either that of [4b, 4d], or of [4a] or [4f] (see page 270) with parameter values which make the arrangement practically indistinguishable from [4b, 4c] or [4b, 4d]. A comparison of the observed intensities and those calculated for these two limiting structures is shown in Table XVI. A zinc sulfide grouping,

Table XVI. Intensities of the Principal Powder Reflections from MnS ($\overline{N}_{Mn} = 23$; $\overline{N}_S = 18$)

Indices	Intensity		
	Observed	Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	0	0.3	10
100(2)	10	10	0.2
110(2)	8	8.8	9.3
113(1)	0	0.2	6.5
111(2)	3	3.6	0.1
100(4)	2	2.0	2.1
133(1)	0	0.1	3.3
120(2)	6	6.0	0.1
112(2)	5.5	4.9	5.1

or a near approach to it is obviously in disagreement with the powder observations. It is thus shown that the atoms of MnS have a sodium chloride arrangement (Figure 167) [4b, 4c], or a grouping indistinguishably close to it.

The length of the edge of the unit cube, as obtained from the calcite comparison spectrum measurement, was found to be $a_0 = 5.214$A°.

Calcium Selenide, CaSe (*1923, 33a*).—A statement of structure, unaccompanied by any data, gives crystals of CaSe a sodium chloride arrangement [4b, 4c] (Figure 167) for which $a_0 = 5.914 \pm 0.006$A°.

Strontium Selenide, SrSe (*1922, 88; 1923, 82a*).—Powder data which have not yet been published are said to indicate a sodium chloride arrangement (Figure 167) of the atoms in this crystal. The length of the edge of the unit cell is said to be $a_0 = 6.234 \pm 0.006$A°.

Barium Selenide, BaSe (*1923, 82a*).—An assignment of structure, also unaccompanied by data, gives crystals of BaSe a sodium chloride arrangement (Figure 167) for which $a_0 = 6.616 \pm 0.006$A°.

Zinc Selenide, ZnSe (*1923, 33b*).—Crystals of ZnSe are said to have cubic symmetry and a zinc sulfide arrangement [4b, 4d] of their atoms

(Figure 174). The length of the edge of the unit cube is given as $a_0 = 5.651 \pm 0.007$A°. Published data are lacking.

Niccolite, NiAs (1923, 1).—Crystallographic information assigns crystals of NiAs to the hexagonal system; but different classes of symmetry have been chosen and different axial ratios suggested.

Laue photographs showed holohedral hexagonal symmetry and corresponded to an axial ratio of $a : c = 1 : 1.430$. Powder photographs also agreed with this axial ratio. If the crystals from which the Laue photographs were prepared were not twinned specimens, then it must be concluded that the symmetry of this crystal is that of one of the classes 6d, 6e, 6D or 6Di. These Laue photographic data permit a unit cell containing two molecules and having the dimensions $a_0 = 3.57$A° and $c_0 = 5.10$A°. The observations, from both the powder and Laue photographs, that planes with indices $hk \cdot (2m + 1)$, where $2h + k = 3p$ and m and p are any integers including zero, are absent would then limit possible structures to the three atomic arrangements which have already been considered for ZnO. As in the previous instance the value of the variable parameter does not influence the intensities of reflections for which $l = 0$; they are therefore the most satisfactory diffractions to use in choosing between the possible arrangements. Calculations of intensity for planes of this sort [using $(d/n)^2$ instead of $(d/n)^{2.35}$ in expression (26)] are shown in Table XVII. The previously designated structure [g] (Figure 175)

[g] Nickel atoms: $00v$; $0, 0, v + \frac{1}{2}$,
Arsenic atoms: $\frac{1}{3}\frac{2}{3}0$; $\frac{2}{3}\frac{1}{3}\frac{1}{2}$.

is in moderate agreement with the observed intensities of this table; the

TABLE XVII. INTENSITY DATA UPON POWDER REFLECTIONS FROM NiAs WHICH HAVE $l = 0$

INDICES	Observed	INTENSITY Calc. for [e]	Calc. for [f]	Calc. for [g]
10.0(1)	1	6.14 units	3.64 units	0.32 units
11.0(1)	4	5.85	5.85	5.85
10.0(2)	0	0.98	0.58	0.05
21.0(1)	0	1.62	0.96	0.08
10.0(3)	4	2.61	2.61	2.61

other structures seem improbable. If v is taken as $\frac{1}{4}$, structure [g] accounts for the absence of certain Laue reflections and at the same time meets the requirements of a rule of constant atomic radii. Largely for this latter reason it has been supposed to be the probably correct atomic arrangement for NiAs.

It is difficult to decide what likelihood there is of this structure being correct. The published data appear to fit it better than they do the other

possibilities but they are scarcely numerous enough to permit of a final conclusion. In view of the inaccuracies of an hypothesis of constant

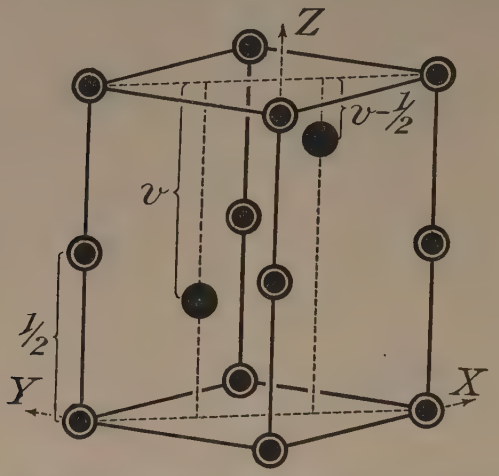


FIG. 175.—The unit cell of one possible arrangement, [g], of the atoms in crystals of NiAs. The axes of reference for this unit have been translated from their positions for the text description of this arrangement until the coördinates have become: nickel atoms at 000 and 00½; arsenic atoms at ⅓⅔ v̄ and ⅔, ⅓, ½–v.

atomic radii (page 399), arguments based upon it for the determination of atomic arrangements cannot receive great weight. It therefore would appear that additional experiments are needed before arrangement [g] can be accepted as the probably true one.

Disulfides, etc.

Pyrite, FeS_2.—Crystals of the pyrite modification of FeS_2 are cubic with the symmetry characteristics of the paramorphic hemihedral class Ti.

Spectrometer measurements (*1914*, 12) upon the (100), (110) and (111) faces and Laue photographs (*1914*, 19, 20) are available. The Laue photographs are strongly hemihedral; hence the symmetry of atomic arrangement in pyrite must be that of either T or Ti. Reflections with all odd, two even and one odd and two odd and one even indices all are found in the first order region of Laue photographs. Consequently the fundamental lattice is Γ_c, the simple cubic lattice. The spectrum observations show that $m/n^3 = 4$; no evidence has been reported to show that m is greater than four. If it is assumed that in accord with the crystallographic information the symmetry is actually hemihedral, and not tetartohedral, only atomic arrangement [4b, 8h] remains possible.

If arrangement [4b, 8h] is the true one then the spectrometer measurements in different orders indicate that u must be in the neighborhood of

0.4. Proceeding upon the assumption that this structure is essentially right, Laue photographic comparisons with only the most qualitative use of "laws" of scattering have placed the sulfur atoms very near to u = 0.388.

This atomic arrangement

[4b, 8h] Iron atoms: $000;\ \frac{1}{2}\frac{1}{2}0;\ \frac{1}{2}0\frac{1}{2};\ 0\frac{1}{2}\frac{1}{2},$

Sulfur atoms: $uuu;\ u+\frac{1}{2},\ \frac{1}{2}-u,\ \bar{u};\ \bar{u},\ u+\frac{1}{2},\ \frac{1}{2}-u;$
$\frac{1}{2}-u, \bar{u}, u+\frac{1}{2};$
$\bar{u}\bar{u}\bar{u};\ \frac{1}{2}-u,\ u+\frac{1}{2},\ u;\ u,\ \frac{1}{2}-u,\ u+\frac{1}{2}$
$u+\frac{1}{2},\ u,\ \frac{1}{2}-u$

is shown in Figure 176. For pyrite the spectrometer reflections lead to a length of the edge of the unit cube: $a_0 = 5.38A°$.

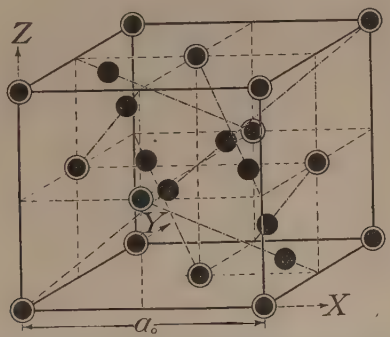


FIG. 176.—The unit cube of the pyrite arrangement [4b, 8h]. The iron atoms, [4b], are represented by the ringed circles, the atoms of sulfur, [8h], by the black ones.

Hauerite, MnS_2 (1914, 19, 20).—Crystals of hauerite are crystallographically isomorphous with those of pyrite. Assuming that the two are also structurally isomorphous and have the atomic grouping [4b, 8h] it is found from a Laue photographic treatment analogous to that given to pyrite that u must be exceedingly close to 0.400. There is no record of a measurement of the length of the edge of the unit cube.

Molybdenite, MoS_2 (1923, 37).—Molybdenite crystallizes in the hexagonal system but there is no certain knowledge of the symmetry class to which it belongs. Crystals of MoS_2 have excellent basal cleavage and with the exception of a couple of prism face reflections, the available spectrum and Laue photographs have been made against or through this face. Such Laue photographs from natural crystals have holohedral hexagonal symmetry; consequently if they arise from untwinned individuals, the symmetry must be that of one of the point groups 6d, 6e, 6D or

6Di. A unit cell built upon the usual crystallographic axial ratio, a : c = 1 : 1.95, conflicts with the Laue data. A similarly oriented unit with twice the axial ratio is in harmony with these and the other data and is taken as the simplest one possible. The dimensions of this unit, which contains two molecules, are as follows:

$$a_0 = 3.15\text{A}^\circ,\ c_0 = 12.30\text{A}^\circ, \text{ corresponding to } a : c = 1 : 3.90.$$

Making the assumption that the two molybdenum atoms are equivalent to one another and that the four sulfur atoms are likewise all equivalent, a reference to the results of the theory of space groups (*1922*, 111) shows that six distinct arrangements are imaginable. Five of them do not fit the Laue data. The sixth meets their general requirements. It is as follows:

[i] Molybdenum atoms: $\frac{1}{3}\ \frac{2}{3}\ \frac{1}{4};\ \frac{2}{3}\ \frac{1}{3}\ \frac{3}{4}$,
Sulfur atoms: $\frac{1}{3}\ \frac{2}{3}\ u;\ \frac{2}{3}\ \frac{1}{3}\ \bar{u};\ \frac{1}{3},\ \frac{2}{3},\ \frac{1}{2} - u;\ \frac{2}{3},\ \frac{1}{3},\ u + \frac{1}{2}$.

For this structure (Figure 177) the relative intensities of 00·1 reflections in different orders are in accord with experiment only when $0.11 < u < 0.15$

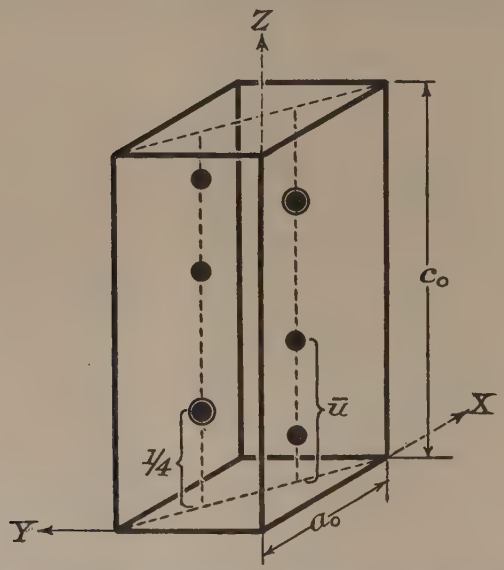


FIG. 177.—The unit cell of the arrangement proposed for the atoms in crystals of MoS_2. The molybdenum atoms are represented by ringed circles, the atoms of sulfur by the black circles.

or when $0.61 < u < 0.65$; but only the second range fits the Laue data. By comparing the intensities of planes with similar spacings and the same type of structure factor the value of u is limited to 0.621 ± 0.004. In this

way only the roughest proportionality is assumed between spacing and reflecting power and no proportionality is demanded between scattering power and atomic number. When this latter "law" is introduced through a comparison of reflections with different structure factors, the agreement with experiment, though still approximate, is not so good.

There is one observation which casts a possible doubt upon the correctness of this structure for MoS_2. Crystals prepared artificially by fusing ammonium molybdate, sulfur and potassium carbonate often show a trigonal as opposed to an hexagonal outline. Such a face development would be expected from a crystal having arrangement [i] only in case the atoms by their own "shapes" gave the crystal a lower symmetry than corresponds to that of their arrangement in space. The more natural explanation is that the specimens used in making the Laue photographs were twinned; but it is stated that no way was found of accounting for the data upon this basis. Again it may be that MoS_2 is dimorphous and that either the artificial crystals are of a different form from those used in the crystal analysis or are pseudomorphs after a high temperature modification. Further experiments to clear up this source of uncertainty are obviously much to be desired.

Cobaltite, CoAsS.—The symmetry and crystal structure of CoAsS present a most puzzling question. Crystallographic information has placed cobaltite in either the tetartohedral or the paramorphic hemihedral class of the cubic system. Laue photographs (*1921*, 72) are said to give data which establish this same symmetry. Nevertheless recent investigations [1] with reflected polarized light deny the cubic character of CoAsS and indicate that at room temperature its crystals are composed of intimately twinned orthorhombic individuals. Such a condition would most probably arise if CoAsS has a high temperature cubic form which during cooling suffers an inversion without change in crystal outline.

If both these optical results and the diffraction measurements are taken at their face values, it seems necessary to conclude that from Laue and spectrum photographs apparently authentic diffraction data can be obtained which do not necessarily have any simple and direct connection with the atomic arrangement in the crystals producing them. This conclusion is of such vital importance to practical crystal analysis that additional X-ray diffraction measurements are needed. In the meantime it is impossible to give final acceptance to either the published diffraction data or to the pyrite-like structure for cobaltite which is deducible from them.

[1] H. Schneiderhohn, Mikroskopische Bestimmung von Erzen, p. 196 (Berlin, 1922).

Chapter XII. The Crystal Structures of Halides, Cyanides, etc.

Monohalides, etc.

This group of crystals has been more completely studied than any other. Practically all simple monohalides and several of the more complex ones have given rise to diffraction data. The structures of crystals of all of the alkali halides (except rubidium fluoride) have been established with a satisfactory degree of correctness; accurate measurements of spacing upon material of known purity are now most needed.

Lithium Hydride, LiH (1922, 11).—Powder photographs have been prepared from LiH. Because of the chemical reactivity of the substance, photographs of Li_2O and LiOH were also made in order to eliminate lines due to them and arising from the decomposition of LiH.

Crystals of lithium hydride are optically isotropic and hence have cubic symmetry. Their powder diffraction lines show that $m/n^3 = 4$. There is no evidence that m is greater than four. The observed lines are those to be expected from either a sodium chloride [4b, 4c] or a zinc sulfide arrangement [4b, 4d]. The wave lengths used in preparing these powder photographs (K-radiation from copper and from chromium) were so long that few reflections could appear. If LiH has the sodium chloride grouping, then it would be anticipated that positive lithium "ions" and negative hydrogen "ions" would be present in its crystals. A comparison of the observed relative intensities and those calculated upon this basis from expression (26) is shown in Table I. There is a better fit with the sodium

Table I. Intensities of the Principal Powder Reflections from LiH ($\bar{N}_{Li} = 2$; $\bar{N}_H = 2$)

	Observed		Intensity	
Indices	Cu Kα	Cr Kα	Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	medium weak	weak	0	10
100(2)	strong	medium strong	10	0
110(2)	medium strong	medium strong	8.8	9.5
113(1)	medium	very strong	0	6.5
111(2)	very weak	strong	3.6	0

chloride arrangement than with the other; because of the large angles of reflection arising from the use of long wave lengths, a closer fit would arise

by using intensity expression (18). It is not, however, to be anticipated that with such simple atoms as these, there would be good agreement with calculations which neglected their electronic distributions. Perhaps the greatest interest in the diffractions from LiH lies in the opportunity offered by the simplicity of its atoms for testing their structures and the laws of scattering. As a result of an effort in this direction several types of atom models are considered to be incompatible with the data and two possible models are suggested. When additional information concerning either the atomic structures or the laws of scattering is available, these data upon LiH will be of still greater importance.

The length of the edge of the unit cube containing four molecules of LiH is found to be $a_0 = 4.10$A°. The atomic arrangement is probably the same as that of sodium chloride [4b, 4c] (Figure 167).

Lithium Fluoride, LiF.—This salt crystallizes in the cubic system. Powder photographs have been obtained with molybdenum (*1919*, 20; *1923*, 33), platinum and copper (*1916*, 5) K-radiation. The observed diffraction lines show that $m/n^3 = 4$; they are the ones to be expected from either the sodium chloride or the zinc sulfide arrangement. The calculated intensities of the reflections from these two groupings upon the assumption that the lithium and fluorine atoms are "ions" are compared with observed intensities in Table II. From these data the zinc sulfide

TABLE II. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM LiF ($\bar{N}_{Li} = 2$; $\bar{N}_F = 10$)

	Intensity			
	Observed		Calculated	
(1)	(2)	(3)	(4)	(5)
Indices	(*1923*, 33)	(*1916*, 5)[1]	For [4b, 4c]	For [4b, 4d]
111(1)	6.7	strong	8.3	10
100(2)	10	strong	10	3.3
110(2)	6.7	medium	8.9	6.6
113(1)	0.5	weak	5.4	6.5
111(2)	0.5	weak	4.0	1.2
100(4)	0.3 —	very weak	2.0	1.4
133(1)	0.2	very weak	2.8	3.3
120(2)	0.4	medium-strong	6.0	2.0
112(2)	0.3	medium-strong	4.9	3.6

structure must be eliminated from further consideration. The agreement of the second set of observed intensities (column 3) with those calculated for the sodium chloride arrangement [4b, 4c] (Figure 167) is on the whole acceptable. The unaccountably low intensity of all but the first three molybdenum reflections (column 2) should be a subject for further investigation.

[1]These intensities refer to reflections of the L $-\alpha$ (unresolved) line of platinum.

It has been thought (*1918*, 11) that the somewhat better fit between experiment and the intensities calculated on the assumption of charged atoms proves the existence of "ions" in this crystal. In the absence of satisfactory knowledge of the laws of scattering, such a conclusion does not seem to be entirely justified.

The length of the edge of the unit cube containing four molecules has been variously determined as $a_0 = 4.14$A° (*1916*, 5), 4.02A° (*1919*, 20) and 4.014 ± 0.008A° (*1923*, 33).

Lithium Chloride, LiCl (*1922, 76; 1923, 33, 71*).—Anhydrous lithium chloride forms crystals with cubic symmetry. The powder photographs to which they give rise show that $m/n^3 = 4$ and display the lines to be expected from the sodium chloride or the zinc sulfide arrangement. The intensity data (Table III) fit better with a sodium chloride structure

TABLE III. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM LiCl ($\bar{N}_{Li} = 2$; $\bar{N}_{Cl} = 18$)

	Intensity			
	Observed		Calculated	
Indices	(*1922*, 76)	(*1923*, 33)	For [4b, 4c]	For [4b, 4d
111(1)	10	10	10	10
100(2)	10	10	8.4	4.2
110(2)	6	5	7.4	5.8
113(1)	4	3.8	6.5	6.5
111(2)	1	0.7	3.1	1.5
100(4)	1	0.4	1.6	1.3
133(1)	—	0.5	3.3	3.3
120(2)	3	0.7	5.0	2.5
112(2)	3	0.5	4.1	3.2

[4b, 4c] (Figure 167). The length of the edge of the unit cube containing four molecules has been given as: $a_0 = 5.17 \pm 0.02$A° (*1922*, 76), 5.143 ± 0.006A° (*1923*, 71) and 5.132 ± 0.006A° (*1923*, 33).

Lithium Bromide, LiBr (*1922, 76; 1923, 33, 71*).—Anhydrous lithium bromide is cubic. Its powder photographs lead to $m/n^3 = 4$ and indicate either the sodium chloride or the zinc sulfide arrangement. As the data of Table IV show, the former fits better with observation. The large intensity of the 113(1) reflection in the third column is probably to be attributed to the presence of an hydration product.

The atomic arrangement in crystals of LiBr is thus probably the sodium chloride structure [4b, 4c] (Figure 167). Two determinations of the length of the edge of the unit cube, made upon the same sample of salt, give $a_0 = 5.48 \pm 0.02$A° (*1922*, 76) and 5.490 ± 0.006A° (*1923*, 33); another estimation yields $a_0 = 5.489 \pm 0.007$A° (*1923*, 71).

Lithium Iodide, LiI.—Anhydrous lithium iodide crystallizes in the cubic system. It is an exceedingly hygroscopic substance that has been prepared with certainty only at temperatures above 300° C. Powder

TABLE IV. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM LiBr ($\overline{N}_{Li} = 2$; $\overline{N}_{Br} = 36$)

	Intensity			
	Observed		Calculated	
(1)	(2)	(3)	(4)	(5)
Indices	(*1922*, 76)	(*1923*, 33)	For [4b, 4c]	For [4b, 4d]
111(1)	10	10	10	10
100(2)	9	10	6.7	4.8
110(2)	6	4	5.9	5.2
113(1)	4	10	6.5	6.5
111(2)	1	2	2.4	1.7
100(4)	—	1.5	1.3	1.2
133(1)	2	4	3.3	3.3
120(2)	—	2	4.0	2.8
112(2)	—	2	3.2	2.9

photographs (*1922*, 76) obtained from samples which were made by grinding a solidified melt of LiI while still hot and immediately sealing the salt in glass tubes gave the lines to be expected from either a sodium chloride or a zinc sulfide grouping for which $a_0 = 6.03$A° (*1923*, 102). As the data of Table V show these intensity data, or any others that could now be obtained, would be incapable of finally deciding between these two arrangements. The probabilities, whatever they may be worth, are of course all in favor of the sodium chloride structure [4b, 4c]. These results are confirmed by other powder photographs which lead to $a_0 = 6.00 \pm 0.007$A° (*1923*, 71).

Another study of powder data (*1923*, 33) has been thought to give LiI the sodium chloride arrangement but with a very different length of edge of the unit cell ($a_0 = 7.074$A°). This appears (*1923*, 102), however, to be an erroneous determination not only because its observed relative intensities (see column 3 of Table V) are not those of the proposed

TABLE V. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM LiI ($\overline{N}_{Li} = 2$; $\overline{N}_{I} = 54$)

	Intensity			
	Observed		Calculated	
(1)	(2)	(3)	(4)	(5)
Indices	(*1922*, 102)	(*1923*, 33)[1]	For [4b, 4c]	For [4b, 4d]
111(1)	10	2	10	10
100(2)	10[2]	10	6.2	5.0
110(2)	6	6.7	5.5	5.1
113(1)	6	1.3	6.5	6.5
111(2)	—	2	2.3	1.8
100(4)	1	1	1.2	1.1
133(1)	3	0.67	3.3	3.3
120(2)	—	1.3	3.7	2.9
112(2)	2	1.3	3.0	2.8

[1] These intensities refer to totally different lines from those measured by column (2).
[2] The excessive intensity of this line is due to the fact that the strongest decomposition line is coincident with it.

structure but because the specimen, grown by desiccation at room temperature, can scarcely have been anhydrous lithium iodide.

Sodium Fluoride, NaF.—Powder photographs (*1922*, 76; *1923*, 33) of this cubic crystal show that $m/n^3 = 4$ and give the lines to be expected from the sodium chloride or the zinc sulfide arrangement. As the data of Table VI make clear the atomic arrangement is like that of sodium chloride

Table VI. Intensities of the Principal Powder Reflections from NaF ($\bar{N}_{Na} = 10$; $\bar{N}_F = 10$)

	Intensity			
	Observed		Calculated	
Indices	(*1922*, 76)	(*1923*, 33)	For [4b, 4c]	For [4b, 4d]
111(1)	absent	0.3	0	10
100(2)	10	10	10	0
110(2)	8	6.7	8.8	9.5
113(1)	—	0.3	0	6.5
111(2)	3	1.3	3.6	0
100(4)	2	0.7	2.0	2.1
133(1)	—	0.3	0	3.3
120(2)	4	1.3	6.0	0
112(2)	—	0.7	4.9	5.2

[4b, 4c] (Figure 167). It is interesting to note that traces of odd order reflections from planes with all odd indices are observable (*1923*, 33): they should be completely absent if the atoms are "ions" and if scattering power were exactly and simply proportional to electron number.

The length of the edge of the unit cube containing four molecules has been found to be $a_0 = 4.61 \pm 0.02$A° (*1922*, 76), 4.68A° (*1921*, 29) and 4.620 ± 0.004A° (*1923*, 33).

Sodium Chloride, NaCl (*1913*, *4*, *8*; *1914*, *12*, *24*; *1915*, *10*, *18*).—It has been customary to have the assumption of a structure for sodium chloride underlie both the accepted wave length of X-rays and the "laws" of scattering. By making the applicability of the quantum theory the basic assumption in wave length determination, as was done in Chapter II, it can be shown that X-ray diffraction data lead to $m/n^3 = 4$. Laue photographs, spectrometer and spectrographic observations and powder photographs have all been made. From none of them is there any evidence that m is greater than four; furthermore they show only those reflections characteristic of arrangements [4b, 4c] and [4b, 4d]. A decision between these two structures can only be made by assuming the roughly qualitative correctness, vouched for by evidence from outside sources and by the agreement which it brings into the mass of X-ray diffraction data, of an approximate proportionality between scattering power and electron number.

Thus on the basis of these fundamental assumptions the experimentally determined atomic arrangement in crystals of sodium chloride is that one (Figure 167) which has been designated as [4b, 4c]. The length of the edge of the unit cube containing four molecules, which usually serves as an accurate standard for X-ray wave length assignments, is taken to be $a_0 = 5.628$A°.

Sodium Bromide, NaBr (*1921, 97; 1923, 33*).—Powder photographs from this cubic crystal show that $m/n^3 = 4$ and give only the lines to be expected from the sodium chloride and zinc sulfide arrangements. Of these two structures the former [4b, 4c] (Figure 167) is clearly the correct one (Table VII). The powder photographs were taken with molybdenum

TABLE VII. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM NaBr ($\bar{N}_{Na} = 10$; $\bar{N}_{Br} = 36$)

	Intensity			
	Observed		Calculated	
Indices	(*1921*, 97)	(*1923*, 33)	For [4b, 4c]	For [4b, 4d]
111(1)	6.7	2.5	6.0	10
100(2)	10	8	10	2.6
110(2)	10	10	8.6	7.2
113(1)	—	3	3.9	6.5
111(2)	—	3	3.7	0.9
100(4)	—	1	1.9	1.6
133(1)	—	1	2.0	3.3
120(2)	—	3	6.0	1.6
112(2)	—	2	4.9	4.0

radiation and the rather poor intensity agreements are perhaps in part to be attributed to the blackening from the secondary characteristic radiation of bromine.

The length of the edge of the unit cube containing four molecules is given as $a_0 = 6.02$A° (*1921*, 29), 5.95 ± 0.01A° (*1921*, 97) and 5.936 ± 0.006A° (*1923*, 33).

Sodium Iodide, NaI.—Powder photographs (*1921*, 97; *1923*, 33) of this cubic crystal prove that $m/n^3 = 4$ and give the lines to be expected from either the sodium chloride or the zinc sulfide arrangement. The agreement (Table VIII) between observed intensities of powder reflections and those calculated for the former grouping is very satisfactory. The sodium chloride arrangement [4b, 4c] hence may be taken as that of the atoms in NaI (Figure 167).

The length of the edge of the unit cube has been found to be $a_0 = 6.50$A° (*1921*, 29), 6.47 ± 0.01A° (*1921*, 97) and 6.462 ± 0.006A° (*1923*, 33).

Potassium Fluoride, KF.—The lines observed upon powder photographs of this cubic crystal are those of either the sodium chloride or the zinc sulfide arrangement. As the data of Table IX show there is satis-

factory agreement between the observed intensities and those calculated for the sodium chloride structure [4b, 4c] (Figure 167).

The length of the edge of the unit cube has been variously determined

TABLE VIII. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM NaI ($\bar{N}_{Na} = 10$; $\bar{N}_I = 54$)

	Intensity.			
	Observed		Calculated	
Indices	(*1921*, 97)	(*1923*, 33)	For [4b, 4c]	For [4b, 4d]
111(1)	9	6.7	8.8	10
100(2)	10	10	10	3.4
110(2)	8	8.3	8.9	6.4
113(1)	5	6.7	5.7	6.5
111(2)	2	3.3	3.7	1.2
100(4)	2	2.5	2.0	1.4
133(1)	3	3.3	2.9	3.3
120(2)	5	5	6.0	2.1
112(2)	5	4.2	4.9	3.6

TABLE IX. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM KF ($\bar{N}_K = 18$; $\bar{N}_F = 10$)

	Intensity			
	Observed		Calculated	
Indices	(*1922*, 76)	(*1923*, 33)	For [4b, 4c]	For [4b, 4d]
111(1)	—	1.5	1.5	10
100(2)	10	10	10	0.8
110(2)	9	8	8.9	8.8
113(1)	—	1	1.0	6.5
111(2)	2	2	3.7	0.3
100(4)	1	1	2.0	1.9
133(1)	—	0.75	0.5	3.3
120(2)	4	2.5	6.0	0.5
112(2)	3	1.5	4.9	4.8

as 5.38A° (*1919*, 20; *1921*, 29), 5.36 ± 0.01A° (*1922*, 76) and 5.328 ± 0.006A° (*1923*, 33).

Potassium Chloride, KCl (*1913, 8; 1914, 24; 1915, 10; 1921, 29; 1923, 33*).—Laue photographs, spectrometer reflections and powder photographs have all been prepared from this cubic crystal. They lead to $m/n^3 = 4$ and none of them gives any evidence pointing to a structure other than either [4b, 4c] or [4b, 4d]. Of these two the sodium chloride arrangement [4b, 4c] (Figure 167) is clearly the correct one (Table X). The scattering powers of chlorine and potassium atoms (or ions) are near enough alike in this crystal so that no odd order reflections have ever been observed, either on Laue or powder photographs.

Two measurements of the length of the edge of the unit cube con-

TABLE X. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM KCl ($\bar{N}_K = 18$; $\bar{N}_{Cl} = 18$)

INDICES	INTENSITY		
	Observed	Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	0	0	10
100(2)	10	10	0
110(2)	6.7	8.8	9.5
113(1)	0	0	6.5
111(2)	2	3.6	0
100(4)	0.7	2.0	2.1
133(1)	0	0	3.3
120(2)	1.7	6.0	0
112(2)	1.0	4.9	5.2

taining four molecules give $a_0 = 6.26$A° and 6.276 ± 0.006A°. The latter was made from powder photographs (*1923*, 33).

Potassium Bromide, KBr (*1913, 8; 1914, 24; 1915, 10; 1921, 29, 97; 1923, 33*).—The lines in the powder photographs of this cubic crystal are those to be expected from either the sodium chloride or the zinc sulfide arrangement. As the data of Table XI indicate, there is excellent accord

TABLE XI. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM KBr ($\bar{N}_K = 18$; $\bar{N}_{Br} = 36$)

INDICES	INTENSITY			
	Observed		Calculated	
	(*1921*, 97)	(*1923*, 33)	For [4b, 4c]	For [4b, 4d]
111(1)	0.5	2	2.1	10
100(2)	10	10	10	1.1
110(2)	10	9	8.8	8.5
113(1)	—	1.5	1.3	6.5
111(2)	2	5	3.6	0.4
100(4)	1	1.5	2.0	1.9
133(1)	—	0.75	0.7	3.3
120(2)	3	6	6.0	0.6
112(2)	3	3	4.9	4.7

between observed intensities and those calculated for the sodium chloride structure [4b, 4c] (Figure 167).

The length of the edge of the unit cube has been determined as $a_0 = 6.60$A° (*1921*, 29), 6.59 ± 0.02A° (*1921*, 97) and 6.570 ± 0.006A° (*1923*, 33).

Potassium Iodide, KI (*1919, 20; 1921, 29, 97; 1923, 28, 33, 94*).—Laue photographs, powder photographs and spectrometer measurements have all been made upon crystals of potassium iodide. They show that for this cubic crystal $m/n^5 = 4$ and give only the planar reflections to be expected from either the sodium chloride or the zinc sulfide arrangement. As the

powder data of Table XII make clear, the sodium chloride structure [4b, 4c] (Figure 167) is the correct one of these two.

TABLE XII. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM KI ($\bar{N}_K = 18$; $\bar{N}_I = 54$)

	Intensity			
	Observed		Calculated	
Indices	(*1921*, 97)	(*1923*, 33)	For [4b, 4c]	For [4b, 4d]
111(1)	8	2.5	4.7	10
100(2)	10	10	10	2.1
110(2)	9	7.5	8.8	7.5
113(1)	4	2.5	3.0	6.5
111(2)	4	3.7	3.6	0.8
100(4)	3	1.9	2.0	1.7
133(1)	—	1.2	1.6	3.3
120(2)	—	5.0	6.0	1.3
112(2)	—	3.7	4.9	4.2

Various determinations of the length of the edge of the unit cube containing four molecules lead to the following results: $a_0 = 7.10$A° (*1919*, 20); 7.11 ± 0.02A° (*1921*, 97), 7.050 ± 0.004A° (*1923*, 33) and 7.064A° (*1923*, 28).

Both characteristic reflections and "anomalous" effects (*1923*, 28, etc.) have been reported from spectrometer studies of potassium iodide crystals (see page 159). Other diffuse, or "hazy," diffraction spots which are not immediately to be attributed to regular planar reflections have been observed upon crystals of potassium iodide (*1923*, 36, 94). They seem related to the systems of radial streaks frequently found from more or less distorted crystals and are in all probability due to some sort of structural imperfections.

Rubidium Fluoride, RbF.—Two attempts have been made to prepare powder photographs of crystalline rubidium fluoride. The first (*1922*, 76) was not successful. Preparations made by fusing RbF were essentially isotropic but they were so hygroscopic that they altered almost immediately upon exposure to the air. A sample used in the second investigation (*1923*, 33) was obtained from solution. It was said to be nicely crystallized—a fact which in itself suggests that the material was not anhydrous RbF. This salt gave powder lines which could be ascribed to reflections from a cubic structure containing one molecule in the unit and thus having the cesium chloride arrangement (see below). The observed intensities of these lines conflict seriously with the intensities calculated for this structure (Table XIII). This disagreement combined with the doubt as to the true chemical composition of the salt investigated makes it highly improbable that the structure of anhydrous RbF has been found.

TABLE XIII. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM RbF ($\bar{N}_{Rb} = 36$; $\bar{N}_F = 10$)

INDICES	INTENSITY Observed (*1923*, 33)	Calculated for [1a, 1b]
100(1)	10	3.6
110(1)	8	10
111(1)	2	1.3
100(2)	1	2.3
110(2)	0.75	2.0
111(2)	0	0.8
120(1)	3	2.2
112(1)	1.5	5.7

Rubidium Chloride, RbCl (*1921, 97; 1923, 33*).—The powder photographs from rubidium chloride show only the lines of the sodium chloride or the zinc sulfide arrangement. As the data of Table XIV show, there

TABLE XIV. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM RbCl ($\bar{N}_{Rb} = 36$; $\bar{N}_{Cl} = 18$)

INDICES	INTENSITY Observed (*1921*, 97)	Observed (*1923*, 33)	Calculated For [4b, 4c]	Calculated For [4b, 4d]
111(1)	—	6.1	2.1	10
100(2)	10	10	10	1.1
110(2)	10	6.7	8.8	8.5
113(1)	—	1.6	1.3	6.5
111(2)	3.3	3.3	3.6	0.4
100(4)	—	2.5	2.0	1.9
133(1)	—	1.6	0.7	3.3
120(2)	3.3	3.3	6.0	0.6
112(2)	—	2.5	4.9	4.7

is acceptable intensity agreement with the first of these [4b, 4c] (Figure 167).

The two determinations of the length of the edge of the unit cube containing four molecules give $a_0 = 6.60$A° (*1921*, 97) and 6.534 ± 0.006A° (*1923*, 33).

Rubidium Bromide, RbBr (*1923, 33*).—The powder photographs of rubidium bromide give only the lines typical of the sodium chloride and zinc sulfide arrangements. The data of Table XV indicate that the sodium chloride grouping [4b, 4c] (Figure 167) is the correct one. The close equality of the scattering powers of the rubidium and bromine atoms in this crystal is attested by the absence of any odd order reflections.

The length of the edge of the unit cube has been found to be $a_0 = 6.93$A° (*1921*, 28) and 6.836 ± 0.006A° (*1923*, 33).

Rubidium Iodide, RbI.—Powder photographs (*1923*, 33) show only the lines of the sodium chloride and zinc sulfide arrangements. Though the

intensity agreements are none too good (especially in the much too rapid decrease of intensity with spacing shown by one set of measurements) it is clear (Table XVI) that the atomic grouping is that of sodium chloride [4b, 4c] (Figure 167).

TABLE XV. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM RbBr ($\overline{N}_{Rb} = 36$; $\overline{N}_{Br} = 36$)

	Intensity		
	Observed	Calculated	
Indices	(*1923*, 33)	For [4b, 4c]	For [4b, 4d]
111(1)	0	0	10
100(2)	10	10	0
110(2)	6.7	8.8	9.5
113(1)	0	0	6.5
111(2)	2	3.6	0
100(4)	0.7	2.0	2.1
133(1)	0	0	3.3
120(2)	2	6.0	0
112(2)	1.3	4.9	5.2

TABLE XVI. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM RbI ($\overline{N}_{Rb} = 36$; $\overline{N}_{I} = 54$)

	Intensity			
	Observed		Calculated	
Indices	(*1921*, 97)	(*1923*, 33)	For [4b, 4c]	For [4b, 4d]
111(1)	—	1.4	0.7	10
100(2)	10	10	10	0.4
110(2)	10	2.9	8.8	9.1
113(1)	—	0.7	0.5	6.5
111(2)	2.0	1.4	3.6	0.1
100(4)	1.7	0.7	2.0	2.0
133(1)	—	0.7	0.2	3.3
120(2)	3.3	1.4	6.0	0.2
112(2)	2.0	1.4	4.9	5.0

Determinations of the length of the edge of the unit cube have yielded $a_0 = 7.36 \pm 0.02$A° (*1921*, 97), 7.308A° (*1922*, 28), and 7.310 ± 0.008A° (*1923*, 33).

Cesium Fluoride, CsF.—There is some evidence [1] for the existence at room temperatures of two modifications of cesium fluoride. The material used in the only crystal structure investigations (*1922*, 76; *1923*, 33) of this salt was a hygroscopic preparation obtained by cooling from the melt. It was optically isotropic and its density was estimated from measurements of the refractive index. This density and the powder photographic data lead to a value of $m/n^3 = 4$. The observed lines are those to be expected from either the sodium chloride or the zinc sulfide

[1] K. Spangenberg, Zeitsch. f. Krist. *57*, 494 (1922–23).

arrangement. As the data of Table XVII indicate there is good intensity agreement with the demands of the sodium chloride grouping [4b, 4c] (Figure 167).

TABLE XVII. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM CsF ($\bar{N}_{Cs} = 54$; $\bar{N}_F = 10$)

	Intensity			
	Observed		Calculated	
Indices	(*1922*, 76)	(*1923*, 33)	For [4b, 4c]	For [4b, 4d]
111(1)	10	6.7	8.8	10
100(2)	10	10	10	3.4
110(2)	7	10	8.9	6.4
113(1)	6	5.3	5.7	6.5
111(2)	—	2.7	3.7	1.2
100(4)	1	1.3	2.0	1.4
133(1)	—	2.0	2.9	3.3
120(2)		3.3	6.0	2.1
112(2)		1.7	4.9	3.6

The two determinations of the length of the edge of the unit cube, made upon samples of the same preparation, are $a_0 = 6.03 \pm 0.02$A° (*1922*, 76) and 6.008 ± 0.006A° (*1923*, 33).

Cesium Chloride, CsCl (*1921*, *32*; *1923*, *33*).—Cesium chloride and the rest of the cesium halides have a different structure from that of the other alkali halides. The powder data (*1923*, 33) combined with the density of the salt show that $m/n^3 = 1$. No reflections have been found which suggest that m should be greater than unity. There is only one way (*1919*, 24; *1922*, 111) of placing one molecule of CsCl within the unit cube. The coördinates of this structure (Figure 178) are the following:

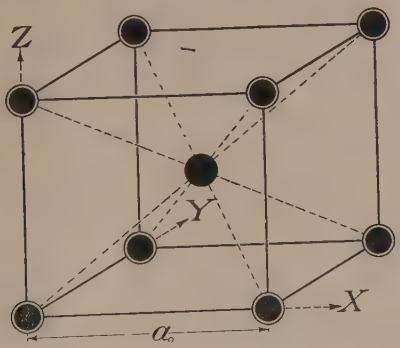


FIG. 178.—The unit cube of the cesium chloride arrangement [1a, 1b]. Atoms of one kind are represented by ringed circles, those of the other sort by the black circles.

[1a, 1b] Cesium (or chlorine) atom: 000,
Chlorine (or cesium) atom: $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

For this arrangement the structure factor of intensity expression (20) has the following values:

$$\left.\begin{array}{l}\text{When n is odd:}\\ \quad\text{If the indices are two odd and one even, } A = \overline{Cs} + \overline{Cl},\ B = 0;\\ \quad\text{If the indices are two even and one odd, or all odd, } A = \overline{Cs} - \overline{Cl},\ B = 0;\\ \text{When n is even:}\\ \quad A = \overline{Cs} + \overline{Cl},\ B = 0 \text{ always.}\end{array}\right\} \quad (39)$$

There is excellent agreement between the observed intensities of reflections and those calculated for this structure (Table XVIII).

TABLE XVIII. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM CsCl ($\overline{N}_{Cs} = 54$; $\overline{N}_{Cl} = 18$)

INDICES	INTENSITY	
	Observed (*1923*, 33)	Calculated for [1a, 1b]
100(1)	1.5	2.8
110(1)	10	10
111(1)	1.0	1.0
100(2)	1.5	2.2
120(1)	1.5	1.7
112(1)	3	5.5
110(2)	1.5	2.0
100(3), 122(1)	1.0	1.1
130(1)	1.5	3.0

Two determinations of the length of the edge of the unit cube containing one molecule give $a_0 = 4.12$A° (*1921*, 32) and 4.118 ± 0.004A° (*1923*, 33).

Cesium Bromide, CsBr.—Powder photographs (*1921*, 97; *1923*, 33) of this cubic substance lead to $m/n^3 = 1$. The lines observed are only those of the simple cesium chloride arrangement [1a, 1b] (Figure 178). The data of Table XIX indicate that there is excellent agreement of the observed intensities with those calculated for this structure.

Determinations of the length of the edge of the unit cube containing one molecule have led to the values: $a_0 = 4.30 \pm 0.01$A° (*1921*, 97), 4.287 ± 0.004A° (*1922*, 28; *1923*, 33).

Cesium Iodide, CsI.—Powder photographs (*1921*, 97; *1923*, 33) of CsI show only the reflections to be expected from a cesium chloride arrangement [1a, 1b] (Figure 178). The observed intensities accord well with those calculated for this atomic grouping (Table XX). The absence of

odd order reflections from planes with either two even and one odd or all odd indices indicates that cesium and iodine atoms have similar scattering powers in this salt.

TABLE XIX. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM CsBr ($\overline{N}_{Cs} = 54$; $\overline{N}_{Br} = 36$)

INDICES	INTENSITY Observed (*1921*, 97)	INTENSITY (*1923*, 33)	Calculated for [1a, 1b]
100(1)	—	0.1	0.5
110(1)	10	10	10
111(1)	—	<0.1	0.2
100(2)	2	1	2.2
120(1)	—	<0.1	0.3
112(1)	7	3.5	5.5
110(2)	2	0.7	2.0
100(3), 122(1)	—	<0.1	0.2
130(1)	3	0.5	3.0

TABLE XX. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM CsI ($\overline{N}_{Cs} = 54$; $\overline{N}_{I} = 54$)

INDICES	INTENSITY Observed (*1921*, 97)	INTENSITY (*1923*, 33)	Calculated for [1a, 1b]
100(1)	0	0	0
110(1)	10	10	10
111(1)	0	0	0
100(2)	2	4.0	2.2
120(1)	0	0	0
112(1)	8	8.0	5.5
110(2)	1	2.5	2.0
100(3), 122(1)	0	0	0
130(1)	4	3.0	3.0

Determinations of the length of the edge of the unit cube have led to: $a_0 = 4.55 \pm 0.015$A° (*1921*, 97), 4.58A° (*1921*, 29), 4.558 ± 0.005A° (*1923*, 33) and 4.562A° (*1922*, 24). The last is the result of a spectrometer observation.

The Thallous Halides.—No data have yet been published upon any of the thallous halides. It has, however, been stated that thallous chloride, TlCl, has the same atomic arrangement as cesium chloride [1a, 1b], the length of the edge of the unit cube being $a_0 = 3.85$A° (*1921*, 32).

Cuprous Chloride, CuCl.—Powder photographic data (*1922*, 112) combined with the known density of CuCl give $m/n^3 = 4$. The only observed reflections are those of either the sodium chloride or the zinc sulfide arrangement. In spite of the excessive faintness of the most distant lines —which at least in part is to be attributed to the thick sheet of specimen

used—the intensity data of Table XXI show that the zinc sulfide grouping [4b, 4d] (Figure 174) is the correct one for this crystal.

TABLE XXI. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM CuCl ($\bar{N}_{Cu} = 28$; $\bar{N}_{Cl} = 18$)

INDICES	INTENSITY		
	Observed	Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	10	0.9	10
100(2)	—	10	0.5
110(2)	8	8.8	9.0
113(1)	7	0.6	6.5
111(2)	—	3.6	0.2
100(4)	—	2.0	2.0
133(1)	0.3	0.3	3.3
120(2)	—	6.0	0.3
112(2)	0.1	4.9	5.0

The length of the edge of the unit cube containing four molecules has been given as $a_0 = 5.49$A° (*1922*, 112). Another study of powder photographs, for which no data have been published, leads to $a_0 = 5.36$A° (*1922*, 27). More accurate spacing measurements are needed for this crystal.

Cuprous Bromide, CuBr.—The lines in powder photographs (*1922*, 112) of CuBr are those of either the sodium chloride or the zinc sulfide grouping. Of these two the structure is clearly (Table XXII) the zinc sulfide arrangement [4b, 4d] (Figure 174).

TABLE XXII. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM CuBr ($\bar{N}_{Cu} = 28$; $\bar{N}_{Br} = 36$)

INDICES	INTENSITY		
	Observed	Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	10	0.3	10
100(2)	—	10	0.2
110(2)	8	8.8	9.3
113(1)	6	0.2	6.5
111(2)	—	3.6	<0.1
100(4)	—	2.0	2.1
133(1)	2	0.1	3.3
120(2)	—	6.0	0.1
112(2)	1	4.9	5.1

The length of the edge of the unit cube containing four molecules has been found to be $a_0 = 5.82$A° (*1922*, 112). Another photograph, for which no data have been published, is said to yield $a_0 = 5.75$A° (*1922*, 27).

Cuprous Iodide, CuI.—Two investigations, both based upon powder data, have been made of the structure of this cubic crystal. In one (*1922*,

112) an artificial preparation was used, in the other (*1922*, 3) the mineral marshite. Both photographs agree in giving only the lines to be expected from either the sodium chloride or the zinc sulfide arrangement. The intensity data of Table XXIII are in satisfactory accord with the requirements of the zinc sulfide grouping [4b, 4d] (Figure 174).

TABLE XXIII. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM CuI ($\bar{N}_{Cu} = 28$; $\bar{N}_I = 54$)

	Intensity			
	Observed		Calculated	
Indices	(*1922*, 112)	(*1922*, 3)	For [4b, 4c]	For [4b, 4d]
111(1)	10	2	1.9	10
100(2)	—	0	10	1.0
110(2)	9	3	8.8	8.6
113(1)	8	3	1.2	6.5
111(2)	—	0	3.6	0.4
100(4)	—	1	2.0	1.9
133(1)	2	2	0.6	3.3
120(2)	—	0	6.0	0.6
112(2)	1	3	4.9	4.7

The length of the edge of the unit cell of the artificial CuI has been determined to be $a_0 = 6.10$A°; for marshite (which probably contained a small amount of silver) a_0 was given as 6.02A°. Another statement of structure (*1922*, 27) which agreed with this accepted arrangement but for which no data have been published, gave $a_0 = 6.07$A°.

Silver Chloride, AgCl.—On several occasions it has been stated that crystals of silver chloride, and of silver bromide, have the sodium chloride arrangement of their atoms. No data, however, have been published. Approximate measurements upon the strongest powder reflections [1] from AgCl are shown in Table XXIV. The observed lines are only those of a

TABLE XXIV. DATA UPON THE PRINCIPAL POWDER REFLECTIONS FROM AgCl ($\bar{N}_{Ag} = 46$; $\bar{N}_{Cl} = 18$)

	Spacing		Intensity		
Indices	Obs.	Calc. ($a_0 = 5.56$A°)	Obs.	Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	3.23A°	3.21A°	8	3.6	10
100(2)	2.81	2.78	10	10	1.7
110(2)	1.98	1.96	9	8.9	8.0
113(1)	1.68	1.67	3	2.3	6.5
111(2)	1.60	1.60	3	4.1	0.6
100(4)	1.39	1.39	1	2.0	1.8
133(1)	—	1.27	—	1.2	3.3
120(2)	1.24	1.24	6	6.0	1.0
112(2)	1.13	1.13	5	4.9	4.4

[1] These data are from unpublished observations made in this laboratory by E. W. Posnjak.

sodium chloride or a zinc sulfide arrangement. The 111(1) reflection seems to be too intense; otherwise there is good agreement with the sodium chloride grouping [4b, 4c] (Figure 167).

The following values have been published for the length of the edge of the unit cube containing four molecules: a_0 = 5.56A° (*1921*, 91); 5.52A° (*1922*, 27); 5.540A° (*1923*, 91).

Silver Bromide, AgBr.—Silver bromide crystals have been said to have a sodium chloride arrangement of their atoms but no data have ever been published. Spacing and intensity measurements upon the principal powder lines [1] of AgBr are recorded in Table XXV. The observed reflections

TABLE XXV. DATA UPON THE PRINCIPAL POWDER REFLECTIONS FROM AgBr ($\bar{N}_{Ag}$ = 46; $\bar{N}_{Br}$ = 36)

	Spacing		Intensity		
Indices	Obs.	Calc. (a_0 = 5.78A*)	Obs.	Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	—	3.33A°	0	0.3	10
100(2)	2.90	2.89	10	10	0.2
110(2)	2.04	2.04	9 —	8.9	9.3
113(1)	—	1.74	0	0.2	6.5
111(2)	1.66	1.67	3	3.6	<0.1
100(4)	1.44	1.44	2	2.0	2.1
133(1)	—	1.32	0	0.1	3.3
120(2)	1.29	1.29	6	6.0	0.1
112(2)	1.17	1.18	4	4.9	5.1

are those to be anticipated from either the sodium chloride or the zinc sulfide arrangement. Their intensities are in excellent agreement with the requirements of the sodium chloride structure [4b, 4c] (Figure 167).

Statements of the length of the edge of the unit cube are a_0 = 5.78A° (*1921*, 91; *1922*, 27) and 5.768A° (*1923*, 91).

Silver Iodide, AgI.—Silver iodide presents an interesting and somewhat puzzling case for which the experimental data from different sources are not yet complete and in satisfactory agreement with one another. Crystals of AgI occur in nature and can be grown to a considerable size in the laboratory; they are optically uniaxial and from a study of their face development they have been supposed to be crystallographically isomorphous with zincite (ZnO). Laue photographs (*1922*, 3) substantiate this conclusion but recent powder measurements (*1923*, 91) upon precipitated silver iodide seem to show that a second, presumably cubic, modification is present. Above 146° C AgI is known to be isotropic and it would be simplest to suppose that under conditions of rapid precipitation this "high temperature" form appears at room temperature as an unstable

[1] These data are from unpublished observations made in this laboratory by E. W. Posnjak.

phase. The unstable character of this non-hexagonal precipitate modification is indicated by the fact that large hexagonal crystals are grown by digesting the precipitate at temperatures below 146° C. Nevertheless the powder measurements (*1922*, 3) available from the well-known high temperature cubic form do not agree with those of the unstable precipitate modification. The observations upon "high"-AgI (and the earlier photographs (*1922*, 3, 4) upon the hexagonal form), however, are so poorly resolved compared with the recent ones that a more accurate repetition of the high temperature measurements seems desirable.

Hexagonal Silver Iodide.—The best available study (*1922*, 3, 4) of the structure of this form of AgI parallels both in its treatment and its results the previously outlined investigation of zincite (ZnO). The Laue photographs show complete hexagonal symmetry; therefore if the crystals used were untwinned individuals their point group must be 6Di, 6D, 6e or 6d. As in the case of ZnO these Laue photographic data combined with a knowledge of the minimum wave length in the X-ray beam lead to a possible unit containing two molecules and having the approximate axial ratio $a : c = 1 : 1.6$. Assuming this possible unit to be the true one and taking the usual crystallographic assignment to the point group 6e as correct, the same possible arrangements are encountered that were discussed for ZnO. It is a property of these structures that odd order reflections from planes with the indices $hk \cdot (2m + 1)$, where $2h + k = 3p$ and m and p are any integers including zero, shall be absent; no such reflections have been found upon either Laue or powder photographs. The scattering powers of silver and iodine are so nearly alike that it would scarcely be possible to decide between the last two structures [f] and [g]. Accepting for the purposes of approximate calculation an equality in the scattering powers of these atoms it is shown that [e], but not [f] or [g], gives qualitative agreement with the powder data if $u = \pm \frac{5}{8}$. The atomic arrangement thus chosen for AgI (Figure 170) is:

[e] Silver atoms: 000; $\frac{2}{3}\ \frac{1}{3}\ \frac{1}{2}$,
Iodine " : $00u$; $\frac{2}{3}$, $\frac{1}{3}$, $u + \frac{1}{2}$, where $u = \pm \frac{5}{8}$.

The evidence which has recently been adduced (*1923*, 91) to show the existence of a cubic modification in precipitated AgI subjects parts of this earlier determination of structure to grave criticism. If, as these new data indicate, the stable hexagonal silver iodide is rarely if ever obtained pure by precipitation, then it is highly improbable that the powder data (*1922*, 4) employed in the previous assignment of structure refer to pure hexagonal AgI. Powder measurements upon a preparation containing only a comparatively small amount of the cubic form have, however, been

published (*1923*, 91). The actual criteria used in deciding upon arrangement [e] were the following (*1922*, 3):

For [e]: The reflections 10·4(1), 11·4(1), 10·2(2), 30·4(1), 21·4(1) and 00·1(4) have minimum intensity values at $u = \frac{5}{8}$ (they equal zero if $\overline{Ag} = \overline{I}$).

For [f] and [g] (if $\overline{Ag} = \overline{I}$): The reflections 10·4(1), 10·2(2), 21·4(1) have maximum intensities at $u = \frac{5}{8}$; the other three of the first group,—00·1(4), 11·2(1) and 30·4(1)—have zero intensities for these values of u. The reflections from (00·1) in different orders are the same for these different structures and the complete absence of 00·1(4) in the new photographs suggests that u lies near to $\frac{5}{8}$ rather than to $\frac{1}{2}$. The non-appearance of all of the decisive reflections in the powder photographs of predominantly hexagonal AgI (*1923*, 91) indicates that the previous choice of [e] was correct.

The extent of the agreement between observed intensities and those calculated [see expression (37)] for the simplest reflections from [e] if u is exactly $\frac{5}{8}$ is shown in Table XXVI. The spacing of the planes as well as

Table XXVI. Data upon the Principal Powder Reflections from Hexagonal AgI ($\overline{N}_{Ag} = 46$; $\overline{N}_I = 54$)

Indices	Observed Spacing	Intensity Observed	Intensity Calculated ($u = \frac{5}{8}$)
10.0(1)	3.991A°	7	8.5
Cubic 111(1)	3.749	7	5.0
00.1(2)	3.742		
10.1(1)	3.512	3	1.3
10.2(1)	2.736	2	3.5
11.0(1)	2.296	10	9.5
Cubic 110(2)	2.292		
10.3(1)	2.115	6	10
10.0(2)	—	0	1.6
11.2(1)	1.963	8	6.4
Cubic 113(1)	1.957		

those of strong lines of the coexisting modification are also shown in order that it may be seen which lines will be unduly strengthened by contributions from the cubic form. The observed intensities meet fairly well the demands of the chosen structure; a part of the existing discrepancies may be due to u having a value not exactly equal to $\frac{5}{8}$.

The crystallographically determined axial ratio for the two-molecule unit is a : c = 1 : 1.6392. That found from the best powder measurements (*1923*, 91) is a : c = 1 : 1.633 ± 0.008. From these powder data the length of the side of the base of the unit cell (Figure 170) is given as $a_0 = 4.593$A°; if c = 1.633, the height of this unit will be $c_0 = 7.500$A°.

Cubic Silver Iodide (*1921*, 91; *1922*, 27; *1923*, 91).—It has already been stated that recent experiments (*1923*, 91) indicate the coexistence in precipitated AgI of a form other than the hexagonal one. The conditions of its production have not been investigated but it is said that some of this second modification seems always to be present in precipitates and occasionally it is found practically pure. The powder lines described for this new form are those to be expected from a cubic crystal which has either the sodium chloride or the zinc sulfide arrangement. As the intensity data (*1923*, 91) of Table XXVII show, there is good agreement with

TABLE XXVII. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM CUBIC AgI ($\bar{N}_{Ag} = 46$; $\bar{N}_I = 54$)

INDICES	INTENSITY		
	Observed (*1923*, 91)	Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	10	0.1	10
100(2)	0	10	0.1
110(2)	8	8.9	9.4
113(1)	7	0.1	6.5
111(2)	0	3.6	<0.1
100(4)	1	2.0	2.1
133(1)	3	<0.1	3.3
120(2)	0	6.0	<0.1
112(2)	3	4.9	5.2

the requirements of the zinc sulfide structure [4b, 4d] (Figure 174). These powder photographs lead to $a_0 = 6.493$A° as the length of the edge of the unit cube.

The high temperature modification of AgI is definitely cubic and it seems most natural to identify it with this unstable form. The single study (*1922*, 3) that has been made of powder reflections from high-AgI shows lines which are different from those of the unstable modification and which have been supposed to indicate a cubic structure of great complexity. It will be important to ascertain whether observations with spectrographs of greater resolution will confirm this complex atomic arrangement.

Miersite.—Miersite is a mixed iodide of monovalent copper and silver. The material that was analyzed had the approximate composition 4 AgI·CuI. A powder photograph (*1922*, 3) of some of the analyzed mineral showed the reflections of a zinc sulfide arrangement [4b, 4d]; the length of the edge of the unit cube was found to be $a_0 = 6.35$A°, a value part way between the spacings of CuI and AgI. Miersite thus appears as one of a series of solid solutions of CuI in cubic AgI.

Ammonium Chloride, NH_4Cl.—Ammonium chloride is dimorphous with an inversion temperature of 184.3°C. Both forms are cubic (isotropic) and both have given rise to X-ray diffraction patterns.

"Low" Ammonium Chloride.—This crystalline species is of particular interest because of the conflict which exists between the results of its crystal structure study and its symmetry as deduced from face development and etch-figure data (see page 209). These crystallographic observations have been thought to assign NH_4Cl to the enantiomorphic hemihedral point group O. The X-ray data show (*1922*, 102, 107) that the symmetry of atomic arrangement cannot be O but must be either tetrahedral (Te) or holohedral (Oi) depending upon the distribution of the hydrogen atoms.

Both Laue (*1922*, 107) and powder photographic (*1921*, 9, 84) data are available. The powder photographs show that $m/n^3 = 1$. The Laue photographs have complete cubic symmetry so that the point group must be Te, O or Oi. Neither these photographs nor the powder photographs contain any reflections incompatible with a unit containing one rather than eight molecules. In discussing the structure of CsCl (page 311) it has been pointed out that there is only one way of arranging two different atoms within a unit cube. From an inspection of the space groups giving rise to this grouping for the nitrogen and chlorine atoms it can be seen that the following is the only way of arranging one molecule of NH_4Cl within a unit cube so that all atoms will occupy positions which conform to the symmetry requirements:

Nitrogen atom: 000,
Chlorine " : $\frac{1}{2}\frac{1}{2}\frac{1}{2}$,
Hydrogen atoms: uuu; $\bar{u}\bar{u}u$; $\bar{u}u\bar{u}$; $u\bar{u}\bar{u}$.

This structure has tetrahedral (Te) symmetry. The results of space group theory further show that there is no possible holohedral arrangement containing eight molecules in which all of the chlorine atoms are alike and all of the nitrogen atoms also are alike; neither can a suitable eight molecule structure with enantiomorphic symmetry be found.

In the other instances of an apparent conflict between the symmetry deduced from crystallographic evidence and that found for the atomic arrangement, the crystallographic symmetry has always been the lower. For ammonium chloride, however, the two symmetries are two different *kinds* of a hemihedry. There is only one apparent way out of the conflict between crystallographic and crystal structure data implied in this result. The study of the ammonium alums (see page 361) suggests that in those crystals the positions of the ammonium hydrogen atoms do not conform to the observed symmetry. From this observation it seems probable that in ammonium chloride also the ammonium groups as wholes, rather than their constituent atoms, occupy the positions in space which

determine crystal symmetry. Thus the ammonium group functions crystallographically, as well as chemically, as a single entity.

From the existing diffraction data it must be concluded that the nitrogen (as centers of ammonium groups) and chlorine atoms of the low temperature form of ammonium chloride have the cesium chloride arrangement [1a, 1b] (Figure 178). The agreement between the observed intensities of powder lines (*1921*, 9) and those calculated for this structure (neglecting the hydrogen atoms) is excellent (Table XXVIII). Two determinations of the length of the edge of the unit cube are: $a_0 = 3.88$A° (*1921*, 84) and 3.859A° (*1921*, 9).

TABLE XXVIII. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM LOW-NH_4Cl($\bar{N}_N = 7$; $\bar{N}_{Cl} = 18$)

	Intensity		
	Observed		
Indices	(*1921*, 9)	(*1921*, 84)	Calc. for [1a, 1b]
100(1)	—	medium-strong	2.2
110(1)	10	strong	10
111(1)	1	weak	0.8
100(2)	2	medium	2.2
120(1)	1.5	medium	1.3
112(1)	3	strong	5.5
110(2)	1.5	medium-strong	2.0
122(1), 100(3)	1	medium	0.8
130(1)	1.5	strong	3.1

"High" Ammonium Chloride (*1921*, 9).—Powder photographs of the high temperature modification, taken at + 250° C, lead to $m/n^3 = 4$. The observed lines are only those of the sodium chloride or the zinc sulfide arrangement. From the intensity data of Table XXIX it is apparent that a zinc sulfide structure is impossible but that except for a somewhat too great intensity of reflection in odd orders from planes with all odd

TABLE XXIX. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM HIGH-NH_4Cl ($\bar{N}_N = 7$; $\bar{N}_{Cl} = 18$)

		Intensity	
Indices	Observed	Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	—	4.0	10
100(2)	10	10	1.7
110(2)	10	8.9	7.9
113(1)	5	2.3	6.5
111(2)	5	4.0	0.6
100(4)	2	2.0	1.8
133(1)	4	1.2	3.3
120(2)	4	6.0	1.0
112(2)	3	4.9	4.4

indices, there is a good fit with the sodium chloride grouping (Figure 167). Again in this instance the hydrogen atoms introduce difficulties. If they occupy positions which agree with the observed cubic symmetry, the crystal class cannot be holohedral. Two arrangements then are possible for the chlorine and nitrogen atoms: One, [4a], is derived from the space groups T−1 and Te−1, the other, [4f], from the group T−4. Their coördinate positions are

[4a] uuu; ūūu; ūuū; uūū, where $u_N \neq u_{Cl}$.
[4f] uuu; $u + \frac{1}{2}, \frac{1}{2} - u, \bar{u}$; $\bar{u}, u + \frac{1}{2}, \frac{1}{2} - u$; $\frac{1}{2} - u, \bar{u}, u + \frac{1}{2}$, where $u_N \neq u_{Cl}$.

These atomic arrangements can give the observed powder data only when u has such values that they approach very close to the sodium chloride structure itself; for [4a] therefore u_N and u_{Cl}. could not deviate appreciably from $\frac{1}{4}$ and $\frac{3}{4}$, for [4f] they would practically equal 0 and $\frac{1}{2}$. For either [4a] or [4f] there are various ways of grouping the hydrogen atoms. Similar approaches to a sodium chloride arrangement can also be obtained with structures containing 32 molecules within the unit cube. In accordance with the results upon the ammonium alums and the low temperature form of NH_4Cl, however, it seems more probable that the hydrogen atoms do not occupy positions required by the observed symmetry; "high" NH_4Cl would thus be a simple sodium chloride grouping (Figure 167) of chlorine atoms and ammonium groups. The length of the edge of the unit containing four molecules has been found to be $a_0 = 6.533$A° at 250° C.

Ammonium Bromide, NH_4Br.—Like ammonium chloride, ammonium bromide has two cubic modifications; the inversion temperature is 137.8°C. Powder photographs have been produced from both forms.

"Low" Ammonium Bromide.—Ammonium bromide at room temperature presents a case which seemingly is strictly analogous to that of the low temperature NH_4Cl. Powder photographic data (*1921*, 9, 84) lead to $m/n^3 = 1$ and give no reflections corresponding to a value of m greater than unity. The nitrogen and bromine atoms thus should have the cesium chloride arrangement (Figure 178); the intensities (Table XXX) calculated upon this basis are in excellent agreement with observation. As with NH_4Cl it is probable that the hydrogen atoms do not have fixed positions which meet the demands of a cubic symmetry.

The length of the edge of the unit cube containing one molecule has been given as $a_0 = 4.07$A° (*1921*, 84) and 3.988A° (*1921*, 9).

"High" Ammonium Bromide.—Powder photographs (*1921*, 9) of NH_4Br taken at 250° C show only the lines of either a sodium chloride or a zinc sulfide arrangement. Except for too intense reflections from

odd orders of planes with all odd indices, the experimental data are in satisfactory accord (Table XXXI) with the requirements of a sodium chloride grouping (Figure 167) of the nitrogen and bromine atoms. The problem of the positions of the hydrogen atoms is identical with that discussed under the high temperature form of NH_4Cl.

TABLE XXX. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM LOW-NH_4Br ($\overline{N}_N = 7$; $\overline{N}_{Br} = 36$)

INDICES	INTENSITY Observed (*1921*, 9)	Calc. for [1a, 1b]
100(1)	—	5.2
110(1)	10	10
111(1)	2	1.9
100(2)	2	2.2
120(1)	4	3.1
112(1)	4	5.5
110(2)	2	2.0
122(1) } 100(3) }	2	2.0
130(1)	2	3.0

TABLE XXXI. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM HIGH-NH_4Br ($\overline{N}_N = 7$; $\overline{N}_{Br} = 36$)

INDICES	INTENSITY Observed	Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	—	8.5	10
100(2)	10	10	3.3
110(2)	10	8.9	6.5
113(1)	8	5.5	6.5
111(2)	4	3.7	1.2
100(4)	2	2.0	1.4
133(1)	6	2.8	3.3
120(2)	6	6.0	2.0
112(2)	4	4.9	3.6

The length of the edge of the unit cube containing four molecules is found to be $a_0 = 6.90$A° at 250° C.

Ammonium Iodide, NH_4I.—Spectrometer observations (*1917*, 25) as well as powder photographs (*1921*, 9) have been made from ammonium iodide at room temperature. They show, as information from other sources has made probable, that this form of NH_4I corresponds to the high temperature modifications of NH_4Cl and NH_4Br. The data give $m/n^3 = 4$ and there is no experimental evidence that m is greater than four. The observed lines are those of either a sodium chloride or a zinc sulfide arrangement. The scattering power of nitrogen is so insignificant

compared with that of iodine that the available diffraction measurements are incapable of deciding between these structures (Table XXXII). Outside evidence, such as relationships to other halides, appropriately additive interatomic distances and cubic as opposed to dodecahedral cleavage, however, make it quite probable that a sodium chloride-like arrangement

TABLE XXXII. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM NH_4I ($\overline{N}_N = 7$; $\overline{N}_I = 54$)

INDICES	INTENSITY		
	Observed	Calc. for [4b, 4c]	Calc. for [4b, 4d]
111(1)	—	10	10
100(2)	—	9.0	4.0
110(2)	10	8.0	6.0
113(1)	10	6.5	6.5
111(2)	3	3.3	1.5
100(4)	2	1.8	1.3
133(1)	8	3.3	3.3
120(2)	8	5.4	2.4
112(2)	5	4.4	3.3

is the correct one. The questions of the positions of the hydrogen atoms and of the symmetry class of this crystal are the same as those already discussed under "high-NH_4Cl."

Two determinations of the length of the edge of the unit cube containing four molecules are $a_0 = 7.20A°$ (*1917*, 25) and $7.199A°$ (*1921*, 9).

Phosphonium Iodide, PH_4I (*1922*, *33*).—Crystals of PH_4I have tetragonal symmetry; but their axial ratio has never been measured. Both spectrum and Laue photographic observations have been made. Spectrum reflections from the base and from a prism face [the crystallographic (110)] show $a : c = 1 : 1.031$ as a possible axial ratio. The smallest unit developed from this ratio has the dimensions $a_0 = 4.48A°$, $c_0 = 4.62A°$ and contains one molecule. The lowest wave length in the X-ray beam used in making the Laue photographs was 0.23A°. Observed spots calculated upon the basis of this one-molecule unit give values of $n\lambda$ as low as 0.15A°; this unit and others differing from it only by having c_0 integral multiples of 4.62A° are therefore impossible. The diagonal unit for which $a_0 = \sqrt{2} \cdot 4.48A° = 6.34A°$ and $c_0 = 4.62A°$ contains two molecules. It yields no impossible values of $n\lambda$ and therefore has been chosen as the simplest one permitted by the X-ray data. From a consideration of the results of the theory of space groups it is shown that no arrangement without variable parameters is compatible with the Laue experiments. This is true not only for the two-molecule unit but for larger ones containing four or eight molecules.

There are only two ways of arranging two sets of two equivalent positions so that the resulting structure will have one variable parameter. They are:

[j]	Phosphorus (or iodine)	atoms:	$0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$,
	Iodine (or phosphorus)	"	00u; 00ū.
[k]	Phosphorus (or iodine)	"	000; $\frac{1}{2}\frac{1}{2}0$,
	Iodine (or phosphorus)	"	$0\frac{1}{2}$u; $\frac{1}{2}$0ū.

The first of these pairs of arrangements, [j], is eliminated by the absence of reflections from planes having the indices (hk0), where h and k are one even and the other odd. A study of first order reflections for which h and k are one even and the other odd and for which the intensity is dependent only upon the value of l shows that u must be near to either 0.10 or 0.40 for the second pair of structures [k]. First order reflections with the indices hk3, where h and k are both odd, are either absent or extremely faint; calculations of the structure factors of these reflections on the assumption that the scattering powers of phosphorus and iodine atoms are roughly proportional to their atomic numbers strongly favor the following arrangement, which consequently has been chosen as the simplest one possible for PH_4I:

[k′]	Phosphorus atoms:		000; $\frac{1}{2}\frac{1}{2}0$,
	Iodine	"	$0\frac{1}{2}$u; $\frac{1}{2}$0ū.

The value of u seems to lie between 0.39 and 0.41 but can hardly be exactly equal to 0.40. This arrangement is in qualitative agreement with all of the Laue data. Its unit cell is shown in Figure 179. As is true of the

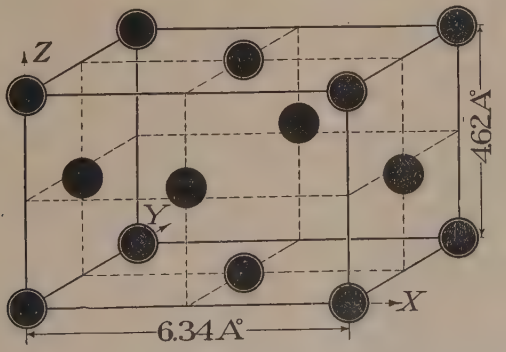


FIG. 179.—The arrangement of the phosphorus (ringed circles) and of the iodine (black circles) atoms in the unit cell of the proposed phosphonium iodide structure [k′].

other ammonium and substituted halides the positions of the hydrogen atoms cannot now be determined. The relation between this structure and that of "low" ammonium chloride, to which it is closely related, will be clear with the aid of Figure 180.

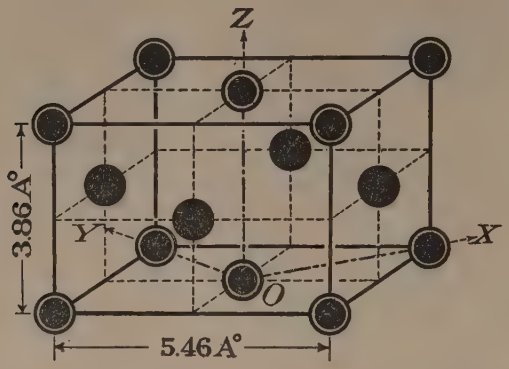


FIG. 180.—A construction cell of the low temperature modification of ammonium chloride, so chosen as to bring out its relation to the phosphonium iodide unit shown in Figure 179. The dot-and-dash lines are the cubic axes of the unit cube of NH_4Cl_2.

Tetramethylammonium Iodide, $N(CH_3)_4I$.—Crystals of this compound have tetragonal symmetry. Spectrometer reflections (*1917*, 25) have been used to give a structure in which the four carbon atoms of a methylammonium group were associated together but not about a central nitrogen atom. This arrangement seemed so improbable that another (*1922*, 67) based upon the space group Di−7 has been proposed. A similar spectrometer technique has proved itself so inadequate, in the case of the alums for instance, that additional experiments are needed before anything definite can be considered to be known about the atomic arrangement in this crystal. Even if the correct space group should have been selected, the other groupings deducible from it have not been finally eliminated.

Potassium Cyanide, KCN (*1921, 26; 1922, 12, 25*).—Reflection data from single crystal faces and Laue photographic measurements have been obtained for this cubic crystal. From the former it is clear that $m/n^3 = 4$; there is no experimental evidence pointing to a value of m greater than four. Only planes with all odd indices reflect in the first order region. This immediately suggests either the sodium chloride or the zinc sulfide arrangement. The intensities of the reflection spectra and the observation (made upon a powder photograph) that 111(1) is weaker than 100(2) eliminate the second type of structure. The problem of the coördinate positions of these atoms then is essentially the same as that

discussed for the high temperature form of ammonium chloride. The two possible structures containing four molecules in the unit are:

[4a] uuu; $u\bar{u}\bar{u}$; $\bar{u}u\bar{u}$; $\bar{u}\bar{u}u$, where $u_K = \frac{1}{4}$ and u_C and u_N lie on either side of $\frac{3}{4}$; and

[4f] uuu; $u + \frac{1}{2}$, $\frac{1}{2} - u$, $\bar{u}$; $\frac{1}{2} - u$, $\bar{u}$, $u + \frac{1}{2}$; $\bar{u}$, $u + \frac{1}{2}$, $\frac{1}{2} - u$,

where $u_K = 0$ and u_C and u_N have values on either side of $\frac{1}{2}$. Besides these there are holohedral groupings [32a] and [32b] (*1922*, 111), which contain 32 molecules and can be made to approach indefinitely close to the sodium chloride arrangement. No selection is now possible between these positions for the carbon and nitrogen atoms; in fact it is not inconceivable that the cyanide group, like the previously discussed ammonium group (see page 320), should function as a structural entity. Making the tentative assumption that [4a] is the correct grouping, it has been shown (*1922*, 12) that best agreement with the data is obtained if the approximate nitrogen and carbon parameters are chosen as 0.80 and 0.70. This result cannot, however, be considered as doing more than indicating in a general way the probable nearness of approach of the nitrogen and carbon atoms. It is also shown that the hypothesis of a single group of outside electrons surrounding both carbon and nitrogen nuclei [1] is not in good agreement with the Laue data interpreted by the prevailing scattering assumptions.

As a result of these studies it must be concluded that in crystals of KCN the potassium atoms and the cyanide groups have a sodium chloride arrangement (Figure 167); the exact distribution of the carbon and nitrogen atoms is not, however, determinable. The length of the edge of the unit cube containing four molecules is given as $a_0 = 6.54$A° (*1921*, 26) and 6.55A° (*1922*, 12).

Dihalides, etc.

Fluorite, CaF_2.—Crystals of CaF_2 are isotropic and apparently have holohedral symmetry. Both spectrometer measurements (*1914*, 12) and powder photographic data (*1921*, 46; *1922*, 37) have been recorded. The published Laue photographs (*1914*, 24; *1915*, 10) have not been analyzed with the thoroughness now possible and consequently are of little value for structure determination. Their apparently holohedral symmetry would however, eliminate atomic arrangements having the symmetry of either T or Ti. The spectrometer and powder data lead to $m/n^3 = 4$ and give no reason for believing that m is greater than four. Two holohedral arrangements [4b, 8e] and [4d, 8d] (see page 279), arise (*1919*, 24; *1922*, 111) from an application of the assumption that the calcium atoms are alike and that the eight fluorine atoms also are alike. Two additional

[1] I. Langmuir, J. Am. Chem. Soc. *41*, 905 (1919).

arrangements can be developed from the space groups O−6 and O−7; they are enantiomorphic and probably are definitely eliminated by the absence of any crystallographic evidence for this sort of hemihedry. Only reflections from planes with all odd indices have been observed in the odd orders. If, as would in all probability be the case, this fact is substantiated by additional powder data and a careful analysis of Laue photographs, it will definitely eliminate not only these two enantiomorphic structures but also [4d, 8d]. These arrangements are all developed from a simple cubic lattice and even though, as in [4d, 8d], the calcium atoms may have the face centered arrangement necessary to give only all odd indices in the odd orders, the scattering power of the fluorine atoms is not negligible. It therefore must be concluded that the best available diffraction data point to the "calcium fluoride arrangement" [4b, 8e] (Figure 171) as the correct one. The extent of the agreement between the observed intensities of powder reflections and those calculated for this structure is shown in Table XXXIII. The structure factor necessary for these calculations has been discussed under CeO_2 (page 281).

TABLE XXXIII. INTENSITIES OF THE PRINCIPAL POWDER REFLECTIONS FROM CaF_2 ($\bar{N}_{Ca} = 18$; $\bar{N}_F = 10$)

INDICES	INTENSITY	
	Observed [1]	Calculated [4b, 8e]
111(1)	medium	4.7
100(2)	?	<0.1
110(2)	strong	10
113(1)	strong	3.1
111(2)	0	<0.1
100(4)	medium	2.2
133(1)	medium-strong	1.6
120(2)	0	<0.1
112(2)	strong	5.5

The length of the edge of the unit cube containing four molecules has been variously given as (*1914*, 12; *1921*, 46; *1922*, 27, 37): $a_0 = 5.40$A°, 5.452A° ± 0.2%, 5.478A° ± 0.2%, 5.455A° ± 0.1% and 5.49A°; all of these except the first are based upon powder data.

Barium Fluoride, BaF_2 (1922, 27).—It has been said that powder photographs show this crystal to have a calcium fluoride arrangement (Figure 171) of its atoms, with $a_0 = 6.20$A°. No data have yet been published.

[1] The reflections to which the data of this column refer were of the Cu K-α line. Because of the large angles resulting from the use of these long X-rays, more than the most qualitative correspondence to the calculated intensities is not to be expected (see page 103).

Cadmium Iodide, CdI_2 (1922, 14).—Crystals of CdI_2 exhibit hexagonal symmetry. Their Laue photographs have complete trigonal symmetry; the symmetry of atomic arrangement must therefore be that of one of the point groups 3e, 3D or 3Di. Making the assumption that the fundamental lattice is hexagonal (Γ_h) rather than rhombohedral (Γ_{rh}), spectrum observations from the base and prism faces yield as a crystallographically conceivable unit one with the axial ratio $a : c = 1 : 1.613$. The dimensions of this unit—$a_0 = 4.24A°$, $c_0 = 6.84A°$—combined with the density show that one molecule would be associated with it. Though the presence of critical absorption limits from both cadmium and iodine must cause great interference, the Laue data seem to agree with this one molecule unit. Reference to the results of space group theory (*1922*, 111) has indicated three arrangements possessed of the necessary symmetry:

[h]	Cadmium atom:	000,	Iodine atoms:	$\frac{1}{3}\frac{2}{3}$u;	$\frac{2}{3}\frac{1}{3}\bar{u}$,
[l]	" "	00u,	" "	$\frac{1}{3}\frac{2}{3}$0;	$\frac{2}{3}\frac{1}{3}$0,
[m]	" "	000,	" "	00u;	0$\bar{0}$$\bar{u}$.

The third, [m], is eliminated by the fact that the third order reflection from (10·0) is stronger than either 10·0(1) or 10·0(2) whereas for this grouping there should be a "normal decline" for all prism face reflections. On the basis of plots of the variation of the structure factor with values of u it is concluded that for no value of u is [l] capable of accounting for the relative intensities of the eight observed orders of reflection from (00·1). These intensity requirements are qualitatively met by arrangement [h] if u lies between 0.23 and 0.253 (with best agreement close to 0.25). The useful Laue data are said to confirm this choice of structure.

It can consequently be concluded that the pyrochroite arrangement [h] (Figure 173), where $0.23 < u < 0.253$, is the simplest one possible for crystals of CdI_2. It is furthermore the only one that can be deduced from an hexagonal unit containing one molecule and having the dimensions $a_0 = 4.24A°$ and $c_0 = 6.84A°$.

Hydrazine Dihydrochloride, $N_2H_6Cl_2$ (1923, 92).—Hydrazine dihydrochloride crystallizes in isotropic octahedrons. Its Laue photographs have a strongly marked hemihedry; the symmetry of atomic arrangement is therefore either T or Ti. The results of spectrum reflections from the (111) face combined with a knowledge of the density yield $m/n^3 = 4$ for molecules of the composition $N_2H_6Cl_2$. There is no evidence from Laue photographs that m should be greater than four. First order reflections from planes with all odd, two odd and one even and two even and one odd indices are all present; the fundamental lattice is therefore the simple cubic one Γ_c. A decision between arrangements developed from the different space groups built upon this lattice can be made from a study

of the first order reflections from planes with one index zero. It is found experimentally that though several planes of the forms [k0l], where k is odd and l is even, appear no reflections are to be found with the indices [0kl], [hk0] or [h0k], where h also is odd. This is a distinctive property of the space group Ti−6. The following arrangement is the only one from Ti−6 which permits a grouping together of the two nitrogen atoms to form, with hydrogen atoms, a hydrazine radical:

[8h] Nitrogen atoms: $uuu;\ u+\frac{1}{2},\ \frac{1}{2}-u,\ \bar{u};\ \bar{u},\ u+\frac{1}{2},\ \frac{1}{2}-u;$
$\frac{1}{2}-u,\ \bar{u},\ u+\frac{1}{2};$
$\bar{u}\bar{u}\bar{u};\ \frac{1}{2}-u,\ u+\frac{1}{2},\ u;\ u,\ \frac{1}{2}-u,\ u+\frac{1}{2};$
$u+\frac{1}{2},\ u,\ \frac{1}{2}-u.$

Chlorine atoms: The same arrangement with u_{Cl} different from u_N.

As usual the positions of the hydrogen atoms cannot be definitely determined. If their positions conform to the symmetry of the crystal as a whole, then they would most naturally be defined by the 24 generally placed equivalent positions of Ti−6 with coördinates which would group six hydrogen atoms around each nitrogen pair. It is assumed, on the basis of the interatomic distances observed in other crystals, that u_N probably is between 0.02 and 0.07 and that u_{Cl} cannot lie outside of the range from 0.11 to 0.44. Upon this basis it is clear that in order to give qualitative agreement with the Laue data u_{Cl} must have a value close to 0.27. The impossibility of assigning any certain value to the scattering power of the light nitrogen atoms prevents the accurate determination of

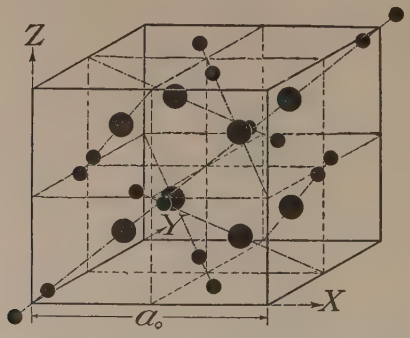


FIG. 181.—The unit cube of the hydrazine dihydrochloride arrangement [8h, 8h].

their positions; nevertheless the best fit with the observations is obtained for u_N around 0.04. The positions of the atoms within the unit cell of this grouping are illustrated in Figure 181. The structure can be thought

of as a somewhat distorted calcium fluoride arrangement of hydrazine (N_2H_6) groups and chlorine atoms. The grouping is strictly analogous to that of the barium atoms and nitrate groups in $Ba(NO_3)_2$.

The length of the edge of the unit cube containing four molecules of $N_2H_6Cl_2$, as determined from a comparison reflection spectrum using the (100) face of calcite as standard, is $a_0 = 7.89A°$.

Tetrahalides, etc.

Tin Tetraiodide, SnI_4 (1923, 35).—Crystals of tin tetraiodide are isotropic with a face development which is distinctly pyritohedral (point group Ti). Laue photographs exhibit a hemihedry which proves that the symmetry of atomic arrangement is either T or Ti. Reflection spectrum measurements from the (111) face combined with the density lead to $m/n^3 = 8$. No obtainable information suggests that m should be greater than eight. First order reflections are present from planes with all odd, two odd and one even and two even and one odd indices. The fundamental lattice must therefore be the simple cubic Γ_c. Criteria are available (Table III of Chapter VII) for selecting between the space groups built upon this lattice in the case of crystals which contain atoms in general positions. These same criteria apply to the special positions which are involved in any placing of eight molecules within the unit cube. From the absence of first order reflections with indices [0kl], [0hk] and [h0k], where h and k are odd and l is even, though [k0l] reflections are present, it may be concluded that the corresponding space group is Ti-6. Inspection of all of the special cases of this space group (*1922*, 111) indicates that the following arrangement is the only one which permits a grouping of iodine atoms about a tin atom:

Tin atoms: The positions of arrangement [8h] (see page 279).

Iodine atoms: Eight atoms with arrangement [8h], where $u_{Sn} \neq u_I$, and the 24 generally equivalent positions of Ti−6 [Ti−6, 24],

$$\begin{array}{l}
xyz;\ x+\tfrac{1}{2},\ \tfrac{1}{2}-y,\ \bar{z};\ \bar{x},\ y+\tfrac{1}{2},\ \tfrac{1}{2}-z;\ \tfrac{1}{2}-x,\ \bar{y},\ z+\tfrac{1}{2};\\
zxy;\ \bar{z},\ x+\tfrac{1}{2},\ \tfrac{1}{2}-y;\ \tfrac{1}{2}-z,\ \bar{x},\ y+\tfrac{1}{2};\ z+\tfrac{1}{2},\ \tfrac{1}{2}-x,\ \bar{y};\\
yzx;\ \tfrac{1}{2}-y,\ \bar{z},\ x+\tfrac{1}{2};\ y+\tfrac{1}{2},\ \tfrac{1}{2}-z,\ \bar{x};\ \bar{y},\ z+\tfrac{1}{2},\ \tfrac{1}{2}-x;\\
\bar{x}\bar{y}\bar{z};\ \tfrac{1}{2}-x,\ y+\tfrac{1}{2},\ z;\ x,\ \tfrac{1}{2}-y,\ z+\tfrac{1}{2};\ x+\tfrac{1}{2},\ y,\ \tfrac{1}{2}-z;\\
\bar{z}\bar{x}\bar{y};\ z,\ \tfrac{1}{2}-x,\ y+\tfrac{1}{2};\ z+\tfrac{1}{2},\ x,\ \tfrac{1}{2}-y;\ \tfrac{1}{2}-z,\ x+\tfrac{1}{2},\ y;\\
\bar{y}\bar{z}\bar{x};\ y+\tfrac{1}{2},\ z,\ \tfrac{1}{2}-x;\ \tfrac{1}{2}-y\,z,\ +\tfrac{1}{2},\ x;\ y,\ \tfrac{1}{2}-z,\ x+\tfrac{1}{2}.
\end{array}$$

All four of the iodine atoms associated with each tin atom thus cannot be crystallographically equivalent; whether this non-equivalence is chemically significant in indicating a difference between the valency bondings of tin is a question which cannot now receive a final answer.

The structure as outlined above possesses five variable parameters; it would therefore not be feasible to attempt a satisfactory determination of their values. The following set of coördinates has been obtained by trial and is said to account qualitatively for the attainable Laue data:

$$u_{Sn} = 0.129;\ u_I = 0.253;\ x = 0.009;\ y = 0.001;\ z = 0.253.$$

The type of atomic arrangement corresponding to this structure is shown in Figure 182. It may be pictured as a grouping of molecules of SnI_4 in

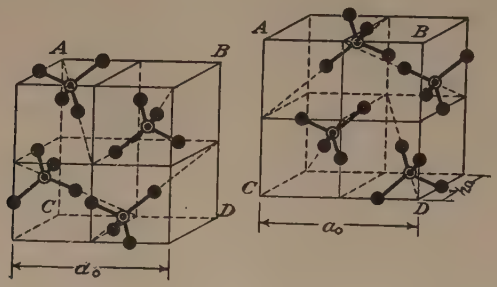


FIG. 182.—Portions of a unit of the tin tetraiodide grouping (after Dickinson). The tin atoms have the positions of the ringed circles; the black circles give possible positions for the iodine atoms.

pairs, about points of a face centered lattice; the pairs of sulfur atoms in pyrite, FeS_2 (Figure 176), are similarly distributed.

The length of the edge of the unit cube containing eight molecules of SnI_4 is determined to be $a_0 = 12.23A°$.

Some spectrum photographs (*1923*, 60), which must have been faint, gave only the reflections of a one-molecule unit. Because of this incompleteness in the experimental data, the partial determination of structure based upon them is necessarily incorrect. Interpreting these spectrum reflections in terms of the true eight-molecule cube, a_0 becomes 12.08A°.

Acid Halides, etc.

Potassium Hydrogen Fluoride, KHF_2 (1923, 16).—Crystals of KHF_2 have tetragonal symmetry, the usually assigned axial ratio being $a : c = 1 : 0.601$. A possible crystal structure has been suggested on the basis of spectrum and Laue photographs. It is found that a unit for which $a_0 = 5.67A°$ and $c_0 = 6.81A°$ ($a : c = 1 : 1.201$) agrees with the Laue data. These measurements combined with the density show that such a unit contains four molecules of KHF_2. The Laue photographs have holohedral symmetry; the symmetry of atomic arrangement is therefore 4d, 4e, 4D or 4Di. Only planes with two odd and one even indices were

found to reflect in odd orders; from this observation it is concluded that the underlying space lattice is body centered. It is thought that the strong fourth and very weak second and sixth order reflections from (001) prove that the potassium and fluorine atoms are exactly in phase for the fourth order reflection and exactly out of phase for the other two. Operating upon this restriction, of unproved validity, it is found that six types of atomic arrangement remain possible. A comparison between the intensity data from Laue photographs and the requirements of these structures shows agreement with only the following:

[n] Potassium atoms: $00\frac{1}{4}$; $00\frac{3}{4}$; $\frac{1}{2}\frac{1}{2}\frac{1}{4}$; $\frac{1}{2}\frac{1}{2}\frac{3}{4}$,

Fluorine " $u, u + \frac{1}{2}, 0$; $\frac{1}{2} - u, u, 0$; $u + \frac{1}{2}, u, \frac{1}{2}$; $u, \frac{1}{2} - u, \frac{1}{2}$; $\bar{u}, \frac{1}{2} - u, 0$; $u + \frac{1}{2}, \bar{u}, 0$; $\frac{1}{2} - u, \bar{u}, \frac{1}{2}$; $\bar{u}, u + \frac{1}{2}, \frac{1}{2}$,

where $u = 0.14 \pm 0.01$.

As usual the positions of the hydrogen atoms are indeterminable; of the three sets of possible positions conforming to the symmetry of the crystal as a whole, the following seems most probable:

Hydrogen atoms: $0\frac{1}{2}0$; $\frac{1}{2}00$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$.

This distribution would place hydrogen atoms between two fluorine atoms with the formation of HF_2 groups. The unit cell of this structure and its relation to the cubic cesium chloride arrangement, which it most closely resembles, is shown in Figure 183.

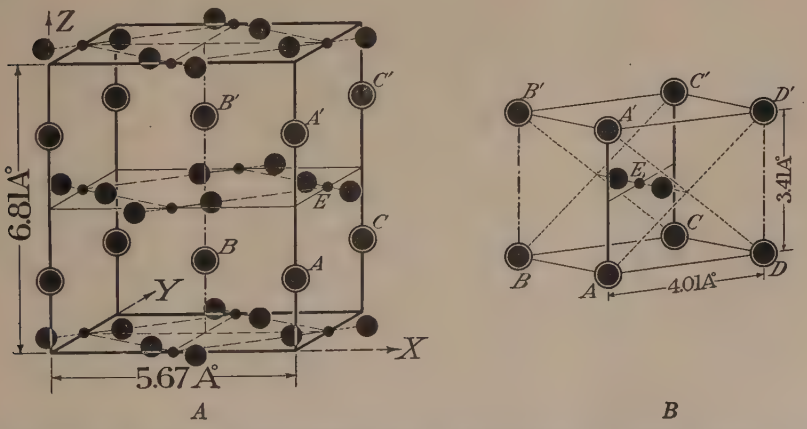


FIG. 183.—The unit cell of the suggested atomic arrangement for KHF_2 is shown at A. The potassium atoms are represented by ringed circles, the fluorine atoms by large black circles. The probable positions of the hydrogen atoms are given by the small black circles. The construction cell of B serves to illustrate the relation that exists between this structure for KHF_2 and the cubic cesium chloride arrangement of Fig. 178.

It is difficult to estimate the probability of correctness for this structure. An arrangement not in conflict with the attainable data has presumably been found but at least one of the assumptions used in deducing it has not received a justification sufficient to permit the conclusion that this atomic arrangement is the only simple one or the simplest one possible for KHF_2.

Sodium Hydrogen Fluoride, $NaHF_2$ (1923, 78).—Crystals of $NaHF_2$ have hexagonal symmetry, presumably belonging to the rhombohedral division of this system. Proceeding upon the assumption that these crystals have the same type of atomic arrangement as that exhibited by $CsCl_2I$, powder photographic data have been used to assign a value to the variable parameter defining the positions of the fluorine atoms in this structure. While it may be true that a similarity in structure exists between these two salts, existing knowledge does not permit any assumption of their structural isomorphism. From an experimental standpoint any study of the structure of non-cubic crystals which does not take into consideration and select between at least some of the geometrically possible unit cells is worthless. For these reasons little weight can be attached to this treatment of sodium hydrogen fluoride.

Hydrates and Ammoniates of Halides, etc.

Nickel Chloride Hexammoniate, $NiCl_2 \cdot 6NH_3$ (1922, 108).—Crystals of this compound are optically isotropic but no crystallographic investigation has ever indicated the symmetry class to which they belong. Spectrum photographs combined with their density give $m/n^3 = 4$; there is no evidence that m is greater than four. Only reflections with all odd indices were found in the first order region. Considering the chemical complexity of the compound this fact is taken to indicate that the lattice underlying the corresponding space group is the face centered Γ_c'. No hemihedry could be observed in the Laue photographs. Since the scattering power of the nickel atoms is not overwhelmingly greater than that of the chlorine and nitrogen atoms it is concluded either that the symmetry of atomic arrangement of the crystal is that of one of the point groups, Te, O or Oi, or that the coördinate sets defining the positions of the nickel, chlorine and nitrogen atoms are deducible from space groups isomorphous with one of these point groups. From this and an inspection of the results of the theory of space groups it follows that the corresponding space group for $NiCl_2 \cdot 6NH_3$ is either Ti−3, O−3 or Oi−5. The attempt to place four molecules of this salt within a unit cube having the symmetry

properties of these space groups shows that the atoms must lie in the following positions:

Nickel atoms: [4b] 000; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$,
Chlorine atoms: [8e] $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}\frac{3}{4}$; $\frac{3}{4}\frac{3}{4}\frac{1}{4}$; $\frac{3}{4}\frac{1}{4}\frac{3}{4}$; $\frac{3}{4}\frac{3}{4}\frac{3}{4}$; $\frac{3}{4}\frac{1}{4}\frac{1}{4}$; $\frac{1}{4}\frac{1}{4}\frac{3}{4}$; $\frac{1}{4}\frac{3}{4}\frac{1}{4}$,
Nitrogen atoms: One of two arrangements which have been designated as [24a] and [24c] (*1922*, 111).

Hydrogen atoms: The positions of the hydrogen atoms cannot of course be found experimentally. If they are situated in accord with the symmetry of the entire crystal, two of the hydrogen atoms of an ammonia group must be crystallographically different from the third. A grouping of three hydrogen atoms about each nitrogen atom is then possible only if the space group is Ti − 3.

Calculations of the appropriate structure factors indicate that if the nitrogen atoms have arrangement [24c] only nickel atoms are reflecting in odd orders; on the other hand if their grouping is that of [24a] nitrogen atoms as well as the atoms of nickel are effective. The Laue data show that under comparable conditions of reflection some first order spots from planes with larger spacings are weaker than those with smaller spacings. This can only occur if the nitrogen atoms are grouped [1] according to [24a]:

Nitrogen atoms: [24a]

$$\begin{array}{l}
u00;\ u+\frac{1}{2},\ \frac{1}{2},\ 0;\ u+\frac{1}{2},\ 0,\ \frac{1}{2};\ u\frac{1}{2}\frac{1}{2};\\
\bar{u}00;\ \frac{1}{2}-u,\ \frac{1}{2},\ 0;\ \frac{1}{2}-u,\ 0,\ \frac{1}{2};\ \bar{u}\frac{1}{2}\frac{1}{2};\\
0u0;\ \frac{1}{2},\ u+\frac{1}{2},\ 0;\ \frac{1}{2}u\frac{1}{2};\ 0,\ u+\frac{1}{2},\ \frac{1}{2};\\
0\bar{u}0;\ \frac{1}{2},\ \frac{1}{2}-u,\ 0;\ \frac{1}{2}\bar{u}\frac{1}{2};\ 0,\ \frac{1}{2}-u,\ \frac{1}{2};\\
00u;\ \frac{1}{2}\frac{1}{2}u;\ \frac{1}{2},\ 0,\ u+\frac{1}{2};\ 0,\ \frac{1}{2},\ u+\frac{1}{2};\\
00\bar{u};\ \frac{1}{2}\frac{1}{2}\bar{u};\ \frac{1}{2},\ 0,\ \frac{1}{2}-u;\ 0,\ \frac{1}{2},\ \frac{1}{2}-u.
\end{array}$$

From a consideration of the effect of the different values of u upon the relative intensities of the observed orders of spectral reflections from (111) it is certain that u_N is near to either 0.25 or 0.50. The structure factor of this arrangement [4b, 8e, 24a] for first order reflections with all odd indices is

$$A = 4\overline{Ni} + 8\bar{N}\ (\cos 2\pi hu + \cos 2\pi ku + \cos 2\pi lu);\ B = 0.$$

The possibility of u being near 0.50 is eliminated and its value in the neighborhood of 0.25 is more accurately found by plotting the variation of A with different values of u for the numerous first order reflections observed

[1] This is true as long as the fundamental assumption (page 101) is maintained that, other things being equal, intensities decrease—in some fashion—with decrease in spacings.

on the Laue photographs. Making use only of cases where planes with larger spacings were weaker than those with smaller spacings this procedure leads to $0.227 < u < 0.245$. If the scattering powers of nickel and nitrogen atoms were proportional to their atomic numbers, which can scarcely be accurately true, u could not be less than 0.24.

The unit cell of this structure is shown in Figure 184. All six of the ammonia groups are equivalent and appear to be most closely related

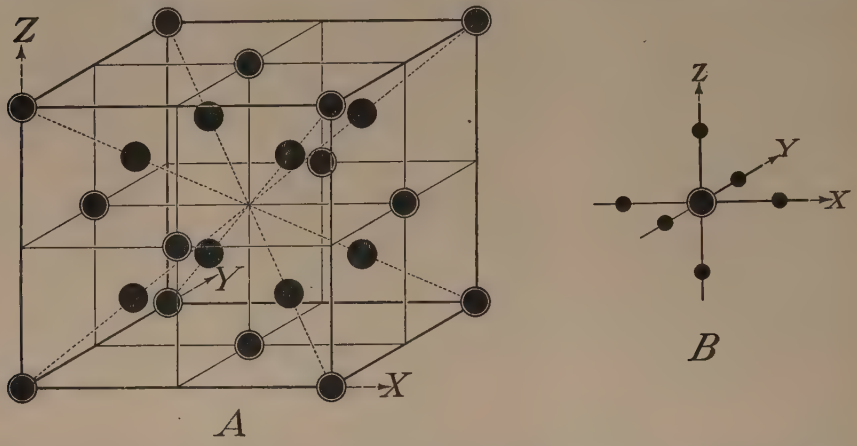


FIG. 184.—The unit cube of the nickel chloride hexammoniate structure [4b, 8e, 24a]. For crystals of $NiCl_2 \cdot 6NH_3$ the nickel atoms are represented by ringed circles and the chlorine atoms by black circles. The positions of the ammonia nitrogen atoms (small black circles) are given if the ringed circles are replaced by the atomic groups of B.

to the nickel atoms. The atoms of chlorine and those of nickel [or $Ni(NH_3)_6$ groups, assuming them to have a physical as well as geometrical existence] have the calcium fluoride arrangement (Figure 171).

A comparison spectrum photograph against a (100) face of calcite as standard gives as length of the edge of the unit cube containing four molecules: $a_0 = 10.09$A°.

Nickel Bromide Hexammoniate, $NiBr_2.6NH_3$ (1922, 108).—Crystals of this salt give X-ray diffraction data which are completely analogous to those of the chloride. By a treatment identical with that just outlined for $NiCl_2 \cdot 6NH_3$ they lead to the same structure [Ni : 4b; Br : 8e; N : 24a]. The length of the edge of the unit cube containing four molecules (Figure 184), as deduced from comparison spectrum measurements, is found to be $a_0 = 10.48$A°. No attempt has been made to estimate the parameter u defining the positions of the nitrogen atoms.

Nickel Iodide Hexammoniate, $NiI_2 \cdot 6NH_3$ (1922, 108).—Crystals of this optically isotropic substance give spectrum and Laue photographs

which are exactly similar to those furnished by the chloride. A treatment like that outlined for the latter yields a nickel chloride hexammoniate arrangement for the iodide. The lesser intensity and smaller number of first order reflections permit only an approximate placing of the nitrogen atoms. From the available reflections of this sort it has been shown that $0.20 < u < 0.25$. Similar considerations upon comparable second order spots seem to favor a value near to 0.24. This same upper value would be necessary with scattering powers of nitrogen and iodine atoms roughly proportional to their atomic numbers.

Comparison spectrum data give as length of the edge of the unit cube containing four molecules (Figure 184) $a_0 = 11.01A°$.

Polyhalides, etc.

Cesium Dichloroiodide, $CsCl_2I$ (1920, 61).—$CsCl_2I$ is said to be dimorphous, crystallizing under some conditions with hexagonal (rhombohedral), under others with orthorhombic symmetry. In the investigation of their crystal structure only twinned rhombohedral specimens which simulated orthorhombic crystals were obtained under conditions intended to produce the orthorhombic form. For this reason the atomic arrangement in only the rhombohedral modification has been studied.

Spectrum measurements from the base combined with the density give $m/n^3 = \frac{1}{2}$ for a unit rhombohedral cell having the shape required by the crystallographically used interaxial angle $\alpha = 98° 22'$. Since crystals having the symmetry of the rhombohedral division of the hexagonal system contain not more than 12 equivalent positions within a unit rhombohedron, reference to Table I of Chapter VII shows that m for such a cell should undoubtedly equal four. Because less simple units would be possible if the fundamental lattice is Γ_h rather than Γ_{rh}, it has been concluded, without, however, any definite proof, that Γ_{rh} is the correct lattice. An interpretation of the Laue data proves that the four molecule cell is not the unit. A cell obtained by taking the face diagonals of this first rhombohedron and containing one molecule of $CsCl_2I$ is satisfactory. The symmetry of the Laue photographs is in accord with the crystallographically assigned symmetry 3Di. If it is assumed that this symmetry class is correctly chosen then a consideration of the results of space group theory shows that the only possible way of arranging one molecule of $CsCl_2I$ within the unit cell is the following (see 3Di−5):

[o] Cesium atom: 000 (or $\frac{1}{2}\frac{1}{2}\frac{1}{2}$),
Iodine " $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ (or 000),
Chlorine atoms: uuu; ūūū.

The scattering powers of the cesium and iodine atoms are so close together that it is impossible to choose experimentally between their alternative positions. By comparing the observed first order reflections from planes having similar spacings with plots of the variation of their calculated intensities with u, it has been shown that u_{Cl} is close to 0.3. If the ratio of the scattering powers of cesium (or iodine) and chlorine were that of their atomic numbers qualitative agreement with the observed data would be obtained only if $0.312 < u < 0.317$. From what is now known of the interatomic distances in other crystals it seems likely that the chlorine atoms are nearer to the iodine atoms than to the cesium atoms (cesium at 000 rather than $\frac{1}{2}\frac{1}{2}\frac{1}{2}$) but this supposition cannot now be tested experimentally.

The unit cell of this atomic arrangement is shown in Figure 185. The grouping is, however, most simply pictured as a sodium chloride structure (Figure 167) in which cesium atoms replace sodium atoms and

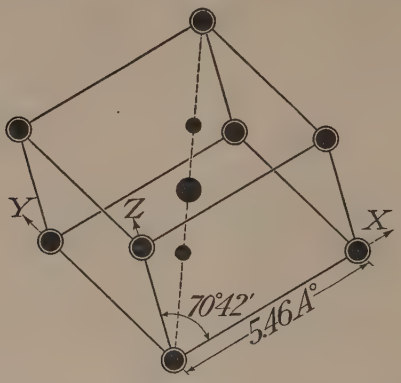


FIG. 185.—The unit rhombohedron of the probable atomic arrangement for cesium dichloroiodide. The chlorine atoms are represented by small black circles. The positions of the cesium and iodine atoms are experimentally indistinguishable, one kind of atom being located at the center, the other at the corners of the unit. It is likely, however, that the iodine atom has the position of the large black circle.

ICl_2 groups replace chlorine atoms and which has been distorted along a trigonal axis until the right angle between coördinate axes has become 98° 22′. The length of the edge of the unit rhombohedron containing one molecule, as determined from spectrum photographs and the angle $\alpha_1 = 70° 42'$, is $a_0 = 5.46$A°.

The structure here deduced is a simple and plausible one which agrees qualitatively with the attainable data. As such it has a certain probability of correctness. It is not, however, proved to be the only simple one that is possible.

Potassium Triiodide, KI_3; Cesium Triiodide, CsI_3; Cesium Dibromiodide, $CsBr_2I$ (1922, 24; 1923, 28, 29).—The first of these crystals is monoclinic, the other two are supposed to be orthorhombic. Spectrometric observations have been made upon a few faces of these crystals using the white radiation from a tungsten tube. As illustrations of resonance reflections from the atoms in crystals these measurements (see for instance Figure 117) are of great interest. Both the data and their treatment are, however, incapable of proving anything definite about the manner of atomic arrangement in crystals with such low symmetry.

Double Halides and Cyanides

Potassium Zinc Cyanide, $K_2Zn(CN)_4$ (1922, 32).—Crystals of this salt, and those of the corresponding cadmium and mercury compounds to be considered subsequently, are optically isotropic and therefore certainly possessed of cubic symmetry. Reflection spectra from the (111) face combined with the density show that $m/n^3 = 8/27$. Laue and spectrum photographic data give no reason for believing that m is greater than eight. Since the symmetry of these photographs is holohedral the symmetry of atomic arrangement must be that of Te, O or Oi. The fact that only planes with all odd indices reflect in the first order region indicates that the fundamental lattice is face centered. Planes of the forms [hkl], where $h = \pm k$, are found to reflect in the first order region; it follows from this (Table III, Chapter VII) that the corresponding space group is Te−2, O−3, O−4, Oi−5 or Oi−7. Eight molecules of $K_2Zn(CN)_4$ cannot be placed within the unit cube of either O−3 or Oi−5. A structure could only be built up from Te−2 by making four of the zinc atoms different from the other four, making all of the potassium atoms alike and causing half of the cyanide groups to be different from the other half. Structures with atoms in arrangement [16a] (*1922*, 111) of Te−2 differ from those developed from Oi−7 in that only the former give second order reflections with the indices 0kl, where k is even and l odd (Table III, Chapter VII). Any arrangement for $K_2Zn(CN)_4$ derived from Te−2 will have five separate sets of atoms grouped according to [16a]. Unless they have such values of u that the resulting structures are in appearance indistinguishable from those to be deduced from O−4 and Oi−7, second orders of [0kl] should be found from such a grouping. Their complete absence in both Laue and spectrum photographs may be taken to eliminate the possibility of distinctive arrangements from Te−2 and to show that the corresponding space group for $K_2Zn(CN)_4$ is Oi−7 (or O−4).

The following two arrangements (*1922*, 111) are possible from Oi − 7 (or O − 4):

Zinc atoms: [8f] 000; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}\frac{3}{4}$; $\frac{3}{4}\frac{1}{4}\frac{3}{4}$; $\frac{3}{4}\frac{3}{4}\frac{1}{4}$,
Potassium atoms: [16b] or [16c],
Carbon atoms: [32b]
uuu; $u+\frac{1}{2}$, $u+\frac{1}{2}$, u; $u+\frac{1}{2}$, u, $u+\frac{1}{2}$; u, $u+\frac{1}{2}$, $u+\frac{1}{2}$;
uūū; $u+\frac{1}{2}$, $\frac{1}{2}-u$, ū; $u+\frac{1}{2}$, ū, $\frac{1}{2}-u$; u, $\frac{1}{2}-u$, $\frac{1}{2}-u$;
ūuū; $\frac{1}{2}-u$, u, $\frac{1}{2}-u$; $\frac{1}{2}-u$, $u+\frac{1}{2}$, ū; ū, $u+\frac{1}{2}$, $\frac{1}{2}-u$;
ūūu; $\frac{1}{2}-u$, $\frac{1}{2}-u$, u; $\frac{1}{2}-u$, ū, $u+\frac{1}{2}$; ū, $\frac{1}{2}-u$, $u+\frac{1}{2}$;
$\frac{1}{4}-u$, $\frac{1}{4}-u$, $\frac{1}{4}-u$; $\frac{3}{4}-u$, $\frac{3}{4}-u$, $\frac{1}{4}-u$; $\frac{3}{4}-u$, $\frac{1}{4}-u$, $\frac{3}{4}-u$; $\frac{1}{4}-u$, $\frac{3}{4}-u$, $\frac{3}{4}-u$;
$\frac{1}{4}-u$, $u+\frac{1}{4}$, $u+\frac{1}{4}$; $\frac{3}{4}-u$, $u+\frac{3}{4}$, $u+\frac{1}{4}$; $\frac{3}{4}-u$, $u+\frac{1}{4}$, $u+\frac{3}{4}$; $\frac{1}{4}-u$, $u+\frac{3}{4}$, $u+\frac{3}{4}$;
$u+\frac{1}{4}$, $\frac{1}{4}-u$, $u+\frac{1}{4}$; $u+\frac{3}{4}$, $\frac{3}{4}-u$, $u+\frac{1}{4}$; $u+\frac{3}{4}$, $\frac{1}{4}-u$, $u+\frac{3}{4}$; $u+\frac{1}{4}$, $\frac{3}{4}-u$, $u+\frac{3}{4}$;
$u+\frac{1}{4}$, $u+\frac{1}{4}$, $\frac{1}{4}-u$; $u+\frac{3}{4}$, $u+\frac{3}{4}$, $\frac{1}{4}-u$; $u+\frac{3}{4}$, $u+\frac{1}{4}$, $\frac{3}{4}-u$; $u+\frac{1}{4}$, $u+\frac{3}{4}$, $\frac{3}{4}-u$.
Nitrogen atoms: Arrangement [32b] with u_N different from u_C.

Reflections from (111) are absent in the second order and stronger in the third than in the first order. By plotting the structure factor of these reflections for the two arrangements and different positions of carbon and nitrogen atoms it was found that the potassium atoms cannot be located according to [16b] and that for the structure using [16c] the effective center of the cyanide group is near 0.35. The arrangement of the potassium atoms in $K_2Zn(CN)_4$ is then:

Potassium atoms: [16c]

$\frac{137}{888}$; $\frac{713}{888}$; $\frac{371}{888}$; $\frac{353}{888}$;
$\frac{151}{888}$; $\frac{115}{888}$; $\frac{511}{888}$; $\frac{555}{888}$;
$\frac{731}{888}$; $\frac{173}{888}$; $\frac{317}{888}$; $\frac{533}{888}$;
$\frac{757}{888}$; $\frac{775}{888}$; $\frac{577}{888}$; $\frac{335}{888}$.

In calculating the structure factors of the two arrangements it is considered that knowledge of interatomic distances derived from studies of other crystals indicates that the distance between the carbon and nitrogen atoms of a cyanide group is between 1A° and 1.5A°. Numerous intensity calculations from the different classes of reflections to be expected from arrangement [8f, 16c, 32b] are all in qualitative accord with experiment. Satisfactory results are obtained if u_N (or u_C) is taken as 0.34 and u_C (or u_N) as 0.40, $[\frac{1}{2}(u_C + u_N) = 0.37]$, but an accurate placing of the carbon and nitrogen atoms can scarcely now be made.

The unit cell of this structure (Figure 186) containing eight molecules of $K_2Zn(CN)_4$ has been found to have a length of edge: $a_0 = 12.54A°$.

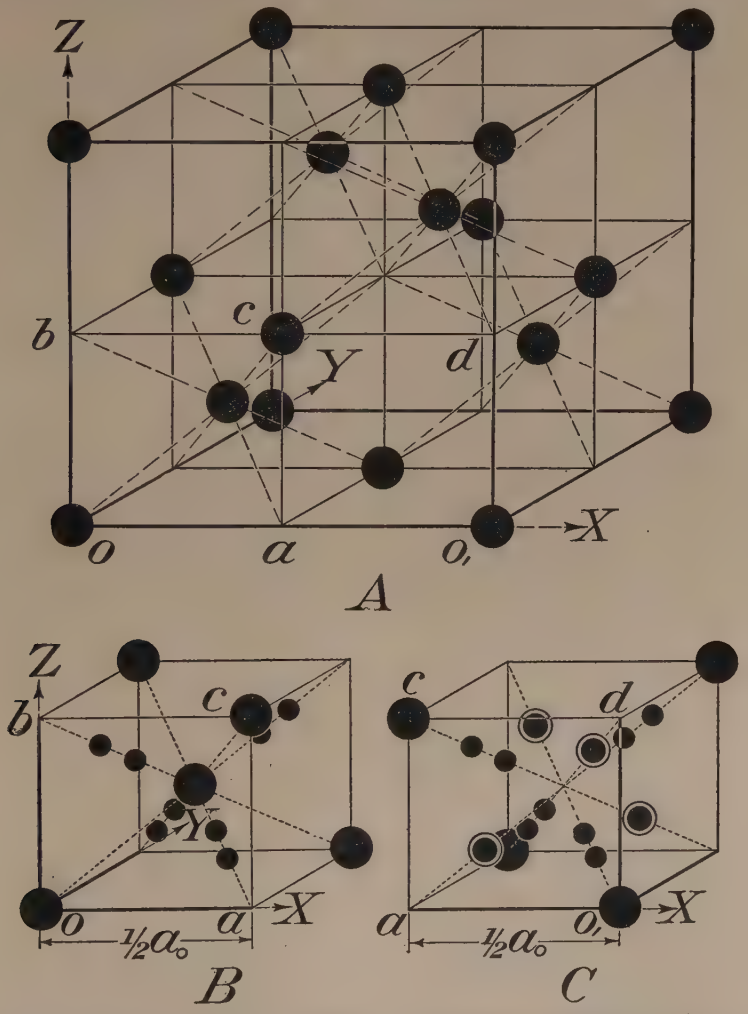


FIG. 186.—The unit cube of the potassium zinc cyanide arrangement [8f, 16c, 32b]. The small sub-units B and C replace alternate eighth size cubes of A. For $K_2Zn(CN)_4$ the potassium atoms [16c] are represented by ringed circles, the zinc atoms [8f] by large black circles, and the carbon and nitrogen atoms (not distinguished from one another) occupy approximately the positions [32b] of the small black circles.

Potassium Cadmium Cyanide, $K_2Cd(CN)_4$ (1922, 32).—Spectra from individual faces and Laue photographs of crystals of $K_2Cd(CN)_4$ furnish data which are strictly analogous to those from $K_2Zn(CN)_4$ and lead in

the manner just outlined to a potassium zinc cyanide structure [8f, 16c, 32b] (Figure 186) with cadmium atoms replacing atoms of zinc. The value of $\frac{1}{2}(u_C + u_N)$ is approximately 0.37. The length of the edge of the unit cube containing eight molecules is $a_0 = 12.84$A°.

Potassium Mercury Cyanide, $K_2Hg(CN)_4$ (1922, 32).—Data from spectrum and Laue photographs of $K_2Hg(CN)_4$ are strictly analogous to those from the two preceding salts. They yield a potassium zinc cyanide arrangement (Figure 186) with atoms of mercury in place of those of zinc. Though effects due to the cyanide groups are less marked than in the zinc salt $\frac{1}{2}(u_C + u_N)$ must be in the neighborhood of 0.37. The length of the edge of the unit cube containing eight molecules is $a_0 = 12.76$A°.

Potassium Chloroplatinite, K_2PtCl_4 (1922, 34).—Crystals of K_2PtCl_4 are tetragonal; their axial ratio is usually stated as a : c = 1 : 0.4161. Data from spectrum and Laue photographs have been assembled. The Laue photographs have holohedral tetragonal symmetry. On the basis of this fact and the absence of crystallographic indications of low symmetry, it is assumed that the symmetry of atomic arrangement is that of the point group 4Di. The simplest unit cell which agrees with the Laue data contains one molecule of K_2PtCl_4 and has the dimensions: $a_0 = 6.99$A°; $c_0 = 4.13$A°, corresponding to the axial ratio a : c = 1 : 0.591. The space group 4Di−1 is the only holohedral group which has the necessary special positions for a unit containing one molecule. Of the numerous possible structures offered by 4Di−1 it is said that the following is the only one which fits the observations:

[p] Platinum atom: 000,
Potassium atoms: $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$;
Chlorine " uu0; $\bar{u}u0$; $u\bar{u}0$; $\bar{u}\bar{u}0$.

By comparing calculations of the structure factor for different orders of (111) with the spectrum photographs, it is shown that u should have a value close to 0.25. Comparisons of the relative intensities of Laue spots with structure factors calculated for different values of u around $\frac{1}{4}$ indicate that u is near to 0.235 and probably lies between 0.233 and 0.238. Qualitative agreement was found between observed relative intensities of reflections from all sorts of planes and those intensities calculated for this structure. The only discrepancies that were encountered were ones which involved the quantitative assumption that the scattering powers of the atoms involved were proportional to their atomic numbers; and these conflicts are eliminated if it is assumed, as indeed seems likely from other sources, that the platinum atoms scatter relatively more than this simple proportionality would imply.

Bearing in mind the assumptions used in its deduction this atomic arrangement [p] is the geometrically simplest one capable of accounting for the observed reflections. Its unit cell is shown in Figure 187.

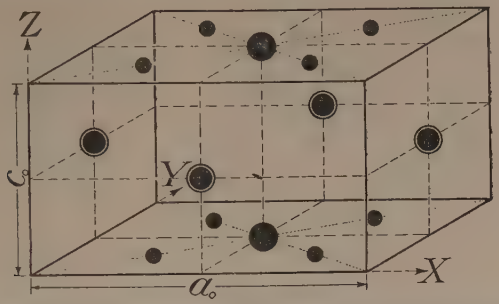


FIG. 187.—The unit cell of the suggested potassium chloroplatinite arrangement [p]. For K_2PtCl_4 the positions of the potassium atoms are given by the ringed circles, the platinum atoms are represented by the large black circles, and the chlorine atoms have approximately the positions of the small black circles.

Potassium Chloropalladite, K_2PdCl_4 (1922, 34).—Spectrum and Laue photographs from crystals of K_2PdCl_4 give data which are like those from K_2PtCl_4 and lead by the same course of reasoning to the same possible structure (with palladium atoms replacing those of platinum). The value of u_{Cl} for this salt is found to be about 0.23. The dimensions of the unit tetragonal prism containing a single molecule (Figure 187) are: $a_0 = 7.04A°$; $c_0 = 4.10A°$, corresponding to the axial ratio $a : c = 1 : 0.582$.

Ammonium Chloropalladite $(NH_4)_2PdCl_4$ (1922, 34).—Crystals of $(NH_4)_2PdCl_4$ give data which are similar to those from the two preceding salts and result in the same type of possible structure. The parameter u for chlorine is close to 0.23. The unit prism containing one molecule (Figure 187) has the following dimensions: $a_0 = 7.21A°$; $c_0 = 4.26A°$, corresponding to the axial ratio $a : c = 1 : 0.591$.

An interesting question is introduced by the attempt to find positions for the hydrogen atoms of the ammonium groups. There is no way of arranging them tetrahedrally about a nitrogen atom so that they will conform to the crystal symmetry. If they actually have such an arrangement then the corresponding space group cannot be 4Di−1 and this crystal must have either lower symmetry or a larger unit cell. It is more probable, however, that as with the ammonium alums, the symmetry of arrangement of the hydrogen atoms (if indeed they have fixed positions with respect to the structure as a whole) is not necessarily that demanded by the observed crystal symmetry.

Potassium Chlorostannate, K_2SnCl_6 (1922, 31).—Spectrum and Laue photographic data from this isotropic crystal are analogous to those from

$NiCl_2 \cdot 6NH_3$ and as a result of the same sort of treatment yield the same atomic arrangement [4b, 8e, 24a]. The positions of the atoms in K_2PtCl_6 are consequently defined by the following coördinate groups:

Tin atoms: Arrangement [4b],
Potassium atoms: Arrangement [8e],

Chlorine atoms: Arrangement [24a]. Intensity comparisons upon the spectrum and Laue photographs and plots of the variation of structure factor (see page 335) with the value of u prove that the observed relative intensities can be qualitatively accounted for only if u is near to 0.245 (and less than 0.25).

The length of the edge of the unit cube containing four molecules (Figure 184) has been found to be $a_0 = 9.96$A°.

Ammonium Chlorostannate $(NH_4)_2SnCl_6$ (*1922, 31*).—Data similar to those from K_2SnCl_6 give the same structure for $(NH_4)_2SnCl_6$ with nitrogen atoms in place of those of potassium. If the hydrogen atoms occupy positions required by the symmetry of the crystal, they will have the coördinate group which has been designated as [32a] (*1922*, 111). The parameter u for chlorine is less than 0.25 and very near to 0.245. No effects due to different values for u_{Cl} could be detected in the data from K_2SnCl_6 and from $(NH_4)_2SnCl_6$.

The length of the edge of the unit cube (Figure 184) is given as $a_0 = 10.05$A°.

Ammonium Chloroplatinate, $(NH_4)_2PtCl_6$ (*1921, 99*).—Spectrum and Laue photographic data lead to a structure identical with that just described for $(NH_4)_2SnCl_6$, if platinum atoms are put in place of atoms of tin. Fewer useful Laue data are available for the platinum than for the tin salt, partly due to the presence of the heavier platinum atoms and partly because of the small size of the crystals used. For this reason it was not possible to exclude experimentally a small region for u_{Cl} around 0.10. Such a close approach of chlorine and platinum atoms is contrary to the existing information concerning interatomic distances. The other, and more probable, position for the chlorine atoms makes u_{Cl} lie somewhere between 0.22 and 0.24. This value for u_{Cl} is, it will be observed, substantially the same as that found for the chlorostannates.

The length of the edge of the unit cube (Figure 184) is stated to be $a_0 = 9.84$A°.

Potassium Chloroplatinate, K_2PtCl_6 (*1922, 84*).—It is reported, without the publication of the powder data upon which the study presumably was based, that crystals of K_2PtCl_6 have the type of atomic arrangement which has been described for K_2SnCl_6, with platinum in place of the tin atoms. The chlorine parameter, however, is said to be around 0.16. Inasmuch

as u_{Cl} has the same value for both the potassium and the ammonium chlorostannates it might be anticipated that $u_{Cl} = \pm 0.24$ for K_2PtCl_6. A more detailed investigation is hence to be desired. No determination has been made of the size of the unit cube.

Ammonium Fluosilicate, $(NH_4)_2SiF_6$ (*1922*, *13*).—This compound is dimorphous—one form being cubic, the other hexagonal in symmetry. Only the cubic modification has yet been investigated. From spectrum and Laue photographic data it has been shown to have the same structure that has been described for $NiCl_2 \cdot 6NH_3$ and for the chloroplatinates and chlorostannates of potassium and ammonium. In $(NH_4)_2SiF_6$ silicon atoms replace tin atoms and fluorine the chlorine atoms of $(NH_4)_2SnCl_6$. The fluorine parameter, u_F, unlike the variable parameters in the other crystals structurally isomorphous with it is given as 0.205.

The length of the edge of the unit cube containing four molecules (Figure 184) is found to be $a_0 = 8.38A°$.

Chapter XIII. The Crystal Structures of Nitrates, Carbonates, Sulfates, Organic Compounds, etc.

Nitrates, Chlorates, Bromates

Sodium Nitrate, $NaNO_3$.—Crystals of sodium nitrate are hexagonal; they appear to have the symmetry of the holohedry of the rhombohedral division (the point group 3Di). Spectrum measurements (*1914*, 12) and Laue photographs (*1920*, 62) have both been made. The holohedral trigonal symmetry of the Laue photographs is in agreement with a symmetry 3Di; but in itself this does not preclude the possibility of the symmetry of atomic arrangement being either 3e or 3D. For crystals having the symmetry characteristics of these point groups unit cells of two different shapes are possible: one is a rhombohedral, the other unit is an hexagonal prism. No method has been devised whereby, at the outset of a determination, a final choice can be made between these units. Nevertheless the following statistical test is possible (*1919*, 32; *1920*, 63). An inspection of the spacing equations of Chapter III shows that in general planes with simple indices have the largest spacings and consequently will give the most intense reflections, other things being equal. Bravais-Miller indices (HK·L), the natural ones for the hexagonal unit, are transformed into Miller indices (hkl), the natural rhombohedral ones, by the following equations:[1]

$$h = 2H + K + L;\ k = K - H + L;\ l = -2K - H + L.$$

If a plane (HK·L) is a simple plane of a rhombohedral lattice the quantities $2H + K + L$, $K - H + L$ and $-2K - H + L$ are each exactly divisible by three. It consequently may be expected that if Miller-Bravais indices are assigned to reflections from a crystal built upon a rhombohedral lattice, the following relation will be maintained for most spots, especially those for which the hexagonal indices are not very simple:

$$\frac{2H + K + L}{3} = \text{integer};\quad \frac{K - H + L}{3} = \text{integer};\quad \frac{-2K - H + L}{3} = \text{integer}.$$

In actual practice it is found that the application of this test divides rhombohedral crystals into two quite distinct groups. Some

[1] See, for instance, P. Groth, Physikalische Krystallographie (Leipzig, 1895), p. 434.

crystals, like pyrochroite, show h, k and l divisible by three in a minority of cases—about as many as occur in truly hexagonal crystals where the underlying lattice is certainly hexagonal. In other crystals, of which sodium nitrate and calcite are examples, the requirements of the preceding relation are met by a large majority of the spots. It has been considered legitimate to take the appearance of such a preponderance of simple rhombohedral reflections as evidence that the fundamental unit is a rhombohedron.

The angle between the crystallographically chosen rhombohedral axes is $\alpha_0 = 102° 42.5'$. Spectra from a (100) face of a rhombohedron developed from these axes show, when combined with the known density, that the smallest cell in this orientation would contain four molecules of $NaNO_3$. The measurements on the Laue photographs indicate, however, that this cell is not a unit cell. The simplest unit rhombohedron compatible with these Laue data is one which contains two molecules and has the angle $\alpha_2 = 48° 6'$ between its axes. The relation between the axes of this new unit and those of the original rhombohedron is shown in Figure 188.

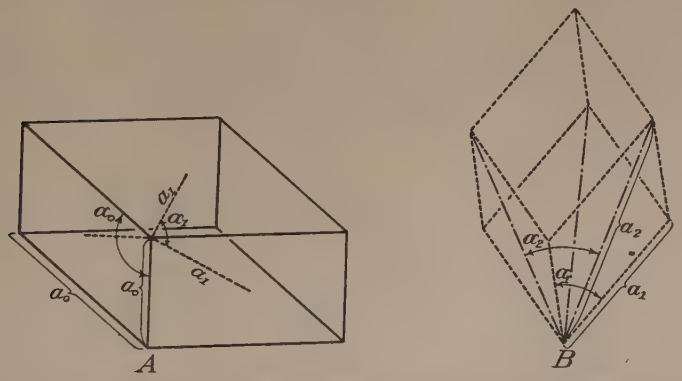


FIG. 188.—The two parts of this figure illustrate the relation between the usual crystallographic axes (those of the cleavage rhombohedron) and the axes of the unit rhombohedron of the sodium nitrate grouping. The length of the edge of the original (cleavage) construction cell is a_0; the edge of the unit rhombohedron is a_2.

Assuming that the symmetry of atomic arrangement is that of 3Di and taking the fundamental lattice to be rhombohedral, two space groups remain possible: 3Di−5 and 3Di−6. It is found that with a few rather weak exceptions all observed first order reflections have too odd and one even indices. This points to an approach to a body centered grouping. Such a structure would be produced from 3Di−5 by giving the sodium (or nitrogen) atoms the coördinates uuu and $\bar{u}\bar{u}\bar{u}$, where $u = \pm \frac{1}{4}$; the nitrogen (or sodium) atoms would occupy the two geometrically unlike

positions 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. This arrangement based upon 3Di−5 is rendered improbable by the fact that it would associate six oxygen atoms equally with each nitrogen atom; on account of the consequent destruction of the NO_3 group of atoms, the space group 3Di−5 is then discarded in favor of 3Di−6.

The following arrangements can be deduced from 3Di−6:

Nitrogen atoms: 000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$,
Sodium " $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{3}{4}\frac{3}{4}\frac{3}{4}$.

Arrangements [q] and [q′]: Nitrogen and sodium atoms as above, [q]; or interchanged [q′]. Oxygen atoms at $\frac{1}{4}\frac{3}{4}\frac{3}{4}$; $\frac{3}{4}\frac{3}{4}\frac{1}{4}$; $\frac{3}{4}\frac{1}{4}\frac{3}{4}$; $\frac{1}{4}\frac{3}{4}\frac{1}{4}$; $\frac{3}{4}\frac{1}{4}\frac{1}{4}$; $\frac{1}{4}\frac{1}{4}\frac{3}{4}$. Calculations of the structure factor of these arrangements show that they should give no two even and one odd effects in the first order. Since such reflections are found these groupings are impossible.

Arrangements [r] and [r′]: Nitrogen and sodium atoms as above, [r]; or interchanged [r′].

Oxygen atoms: uū0; ū0u; 0uū; $\frac{1}{2}-u$, $u+\frac{1}{2}$, $\frac{1}{2}$; $u+\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}-u$; $\frac{1}{2}$, $\frac{1}{2}-u$, $u+\frac{1}{2}$.

The existing data probably do not permit a conclusive experimental decision between [r] and [r′] because the nitrogen and sodium atoms are not enough different in scattering powers. Grouping [r] is nevertheless assumed to be the correct one in order to preserve the nitrate group of atoms.

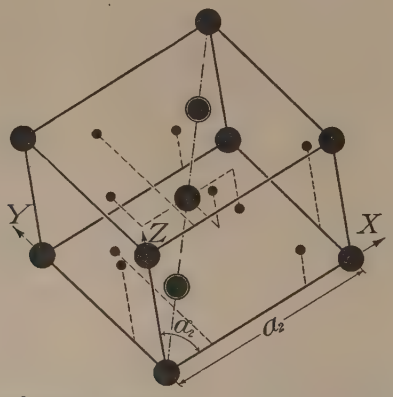


FIG. 189.—The unit rhombohedron of the sodium nitrate, or calcite, grouping of atoms [r]. The sodium atoms are represented by ringed circles; the nitrogen atoms are shown as large, the oxygen atoms as small, black circles.

The spectrometer reflections (*1914*, 12) are said to indicate that u is close to $\frac{1}{4}$. Studies of Laue reflections to which only oxygen atoms were contributing led to the same position through comparisons of the

variation of the structure factor (see page 217 and Figure 145) with changes in u; no evidence could be found for a deviation from exactly $u_o = 0.25$.

This atomic arrangement is the geometrically simplest one which can account qualitatively for all obtainable diffraction data. Its unit cell is shown in Figure 189. The length of the edge of the unit rhombohedron containing two molecules is $a_2 = 6.320A°$; the equal angle [1] between its axes is $\alpha_2 = 48° 6'$. This structure may be conveniently pictured as a sodium chloride grouping (Figure 167) in which nitrate groups replace chlorine atoms and which has been compressed along a trigonal axis normal to the plane of the nitrate groups (Figure 190).

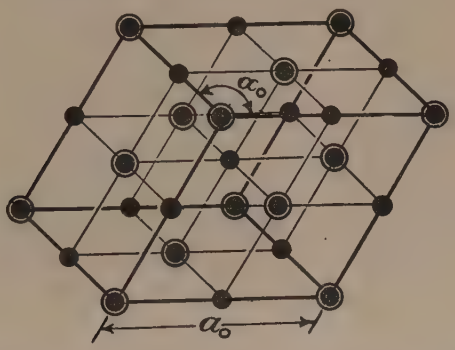


FIG. 190.—The construction cell (A of Fig. 188) of the sodium nitrate structure showing the positions of the nitrogen and sodium atoms and the similarity between this arrangement and the sodium chloride grouping of Fig. 167.

Sodium Chlorate, $NaClO_3$ (1921, 37, 61; 1922, 93, 101; 1923, 52, 55, 56).—Crystals of sodium chlorate are isotropic and therefore cubic. Their face development and the phenomena of circular polarization which they exhibit definitely establish their symmetry as that of the point group T. Spectrometer observations (*1921*, 37), powder photographs (*1921*, 61; *1922*, 93; *1923*, 52) and Laue photographs (*1923*, 55) have all been studied. The spectrometer measurements are reliable because care was taken to eliminate interfering reflections from other faces than the one under examination. These data combined with the density show that $m/n^3 = 4$; there is no evidence to indicate that m is greater than four.

The presence of odd orders of reflection from planes with two even and one odd, two odd and one even and all odd indices shows that the fundamental lattice is the simple cubic Γ_c. The two tetartohedral space groups developed from this lattice are T−1 and T−4. Diffraction

[1] These dimensions are incorrectly stated in reference (*1920*, 63).

effects from atoms in general positions of these two space groups are distinguished (Table III of Chapter VII) only by the absence, for T−4, of odd order reflections from the plane (100). No (100) odd order spectra were observed and it consequently has been concluded that the corresponding space group is T−4.

The following atomic arrangement of four molecules of $NaClO_3$ is the only one possible from this space group:

Sodium atoms: [4f] uuu; $u + \frac{1}{2}, \frac{1}{2} - u, \bar{u}$; $\bar{u}, u + \frac{1}{2}, \frac{1}{2} - u$; $\frac{1}{2} - u, \bar{u}, u + \frac{1}{2}$,

Chlorine " Arrangement [4f] with a different value of u,

Oxygen " [T−4, 12] xyz; $x + \frac{1}{2}, \frac{1}{2} - y, \bar{z}$; $\bar{x}, y + \frac{1}{2}, \frac{1}{2} - z$; $\frac{1}{2} - x, \bar{y}, z + \frac{1}{2}$;
zxy; $\bar{z}, x + \frac{1}{2}, \frac{1}{2} - y$; $\frac{1}{2} - z, \bar{x}, y + \frac{1}{2}$; $z + \frac{1}{2}, \frac{1}{2} - x, \bar{y}$;
yzx; $\frac{1}{2} - y, \bar{z}, x + \frac{1}{2}$; $y + \frac{1}{2}, \frac{1}{2} - z, \bar{x}$; $\bar{y}, z + \frac{1}{2}, \frac{1}{2} - x$.

The five independent and variable parameters possessed by this grouping scarcely permit of a systematic investigation of the atomic positions. Nevertheless several coördinate sets have been suggested as possibilities. One (*1921*, 61; *1923*, 52), based upon powder measurements, has these values:

$u_{Na} = 0.083 = 1/12$; $u_{Cl} = 0.417 = 5/12$; $x = 0.50 = \frac{1}{2}$; $y = 0.417 = 5/12$; $z = 0.306 = 11/36$.

Such an arrangement groups three oxygen atoms about each chlorine atom and thus permits the existence of a chlorate group; the resulting distance between a chlorine and an oxygen atom ($\pm$ 0.91A°) is, however, much less than might be expected from other knowledge of interatomic distances. On the basis of the spectrometer measurements (*1921*, 37) a somewhat different distribution is suggested:

$u_{Na} = 0.08$; $u_{Cl} = 0.43$; $x = 0.30$; $y = 0.59$; $z = 0.47$.

It will be observed that the positions of the sodium and chlorine atoms are practically the same in the two cases; as the unit cells of Figure 191 show, there is a considerable difference in the arrangement of the oxygen atoms. Both structures account fairly well for the observed reflections; it is of interest to remark that the somewhat better fit supplied by the second (spectrometer) set of coördinates occurs for those reflections which, having the same absolute values of h, k and l, give inseparable powder reflections. Laue photographic measurements (*1923*, 55) agree with the

general outlines of these structures; they have been made the basis for a set of coördinates practically identical with the preceding one (*1921*, 37):

$$u_{Na} = 0.071;\ u_{Cl} = 0.429;\ x = 0.301;\ y = 0.593;\ z = 0.473.$$

Still another atomic distribution has been suggested on the basis of powder data (*1922*, 93). For this arrangement the variable parameters are:

$$u_{Na} = 0.056;\ u_{Cl} = 0.408;\ x = 0.608;\ y = 0.639;\ z = 0.500.$$

The chlorine positions in this last structure are practically the same as in the three preceding ones and the sodium atoms are not very differently

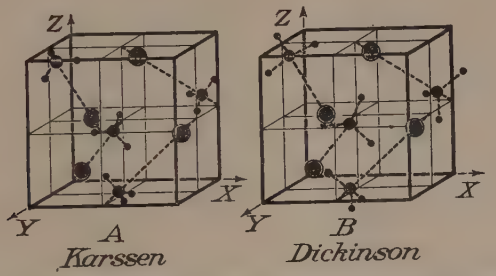


FIG. 191.—Unit cubes of the sodium chlorate structure illustrating the atomic positions chosen by two different investigators. The sodium atoms are represented by ringed circles, the chlorine atoms by large and the oxygen at ms by small black circles. It will be noted that the axes of reference are different from those used in most of the figures of this book.

located. The grouping of the oxygen atoms is, however, unlike that in the other arrangements. It should be noted that the intensity estimations are not the same for the two powder investigations (*1921*, 61; *1922*, 93).

From the foregoing it seems likely that the positions of the chlorine and sodium atoms have been approximately found. It would, however, hardly appear feasible at present to determine uniquely the atomic positions of oxygen.

An attempt to calculate quantitatively the optical rotatory power using one (*1921*, 61) of the above sets of parameters was not successful (*1923*, 46).

The length of the edge of the unit cube containing four molecules has been determined to be: $a_0 = 6.55$A° (*1921*, 61; *1923*, 52); 6.56A° (*1921*, 37); and 6.58A° (*1922*, 93).

Sodium Bromate, $NaBrO_3$.—The crystal structure of $NaBrO_3$ has been investigated using spectrometer data (*1921*, 37) and powder photographs (*1921*, 61; *1922*, 93; *1923*, 52). The measurements are entirely analogous to those from $NaClO_3$ and lead by the same course of reasoning to the "sodium chlorate arrangement" [4f; T—4, 12]. Two sets of suggested

parameters for sodium and bromine are similar and almost the same as the probable values for the chlorate. The conditions for the determinations of the oxygen parameters are not so favorable as in sodium chlorate because of the proportionately great effects of the bromine atoms; consequently still less value can attach to the assigned quantities x, y and z for $NaBrO_3$. These two sets of parameters are:

$u_{Na} = 0.083 = 1/12$; $u_{Br} = 0.417 = 5/12$; $x = 0.50 = \frac{1}{2}$; $y = 0.417 = 5/12$; $z = 0.306 = 11/36$ (the same as for $NaClO_3$, *1921*, 61; *1923*, 52).

$u_{Na} = 0.09$; $u_{Br} = 0.41$; $x = 0.30$; $y = 0.60$; $z = 0.47$ (*1921*, 37).

Another set of coördinates (*1922*, 93) with $u_{Na} = 0.06$, $u_{Br} = 0.408$ and x, y and z different from either of the preceding has also been proposed.

The length of the edge of the unit cube containing four molecules has been given as $a_0 = 6.70$A° (*1921*, 61; *1923*, 52); 6.71A° (*1921*, 37) and 6.72A° (*1922*, 93).

Barium Nitrate, $Ba(NO_3)_2$.—The results of the study of atomic arrangement in this isotropic crystal introduce a difficult crystallographic problem. Investigations of their external symmetry have placed crystals of $Ba(NO_3)_2$ in the tetartohedral class T. Thus positive and negative tetrahedrons are distinguished, though they are usually about equally developed. It has been said [1] that the two tetrahedrons can be distinguished by their pyroelectric properties; on the other hand no piezoelectric effects could be observed and the crystals have never been made to show the phenomena of circular polarization.

Laue and spectrum photographic data (*1917*, 16), which have not been published in detail, and powder measurements (*1922*, 92) seem to point to a structure with pyritohedral (Ti) rather than tetartohedral (T) symmetry. The conflict between these symmetry results is sufficiently marked and the data upon which they are based are, at least potentially, so rich that additional crystallographic and structural studies must be made in order either to reconcile this difference or to establish definitely a conflict between crystallographic and structural symmetries more serious than any thus far encountered.

Laue photographs show a distinct hemihedry so that the symmetry of atomic arrangement must be that of either T or Ti. Both the powder data and the unpublished spectrographic reflections show that $m/n^3 = 4$; and there is no evidence from any source to indicate that m is greater than four. First order reflections are found from planes with two odd and one even, two even and one odd, and all odd indices so that the fun-

[1] W. G. Hankel, Leipziger Abh. *24*, 482 (1899).

damental lattice must be the simple cubic Γ_c. A distinction between such tetartohedral and pyritohedral space groups can be made from a study of planes with one index zero (Table III, Chapter VII). For this purpose powder measurements are worthless except to confirm the presence or absence of odd orders from (100). Laue data have not been published but a few observations, made for another purpose,[1] meet the demands of the space group Ti−6. Only a few [0kl] reflections are found in the first order on account of the relatively great scattering power of the barium atoms. A larger number of such spots would be present in photographs of strontium or calcium nitrates, and any uncertainty which may now exist concerning the choice of Ti−6 could be met by a study of these crystals.

Taking the corresponding space group of barium nitrate as Ti − 6 and knowing that four molecules are contained within the unit cube, reference to the results of the theory of space groups (*1922*, 111) proves that the atoms within the unit cube must have the following coördinate positions:

Barium atoms: [4b] 000; $\frac{1}{2}\frac{1}{2}0$; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$,
Nitrogen atoms: [8h] (see page 330),
Oxygen atoms: [Ti−6, 24] (see page 331).

There are thus four variable parameters in this crystal structure. On the basis of the Laue data it has been said that the following positions are approximately, but only approximately, the correct ones: $u_N = \frac{1}{4}$, $x = \frac{1}{4}$, $y = \frac{1}{4}$, $z = 0$; it can, however, be shown that considerable variations from these parameter values are possible in view of the non-quantitative character of the knowledge of scattering. The powder photographic observations have been used to give definite positions to the nitrogen and oxygen atoms; the results of similar measurements upon the chlorate and bromate of sodium seem to demand the conclusion that such powder data are not now capable of establishing with any approach to certainty the correct positions of all of the atoms in such a crystal as barium nitrate.

It is a necessary consequence of the geometrical equivalence of all of the oxygen atoms of this structure [4b; 8h; Ti−6, 24] that the three oxygen atoms which presumably are grouped about each nitrogen atom are all equally related to it. If as is very probably the case the parameter u_N for the nitrogen atoms (acting as centers of the nitrate groups) is close to $\frac{1}{4}$, this structure may be pictured as of the fluorite type (Figure 171) with NO_3 groups replacing the fluorine atoms.[2]

[1] From unpublished data by the writer.

[2] This arrangement would be even more closely related to hydrazine dihydrochloride $[N_2H_6Cl_2]$ (Figure 181), if barium atoms are substituted for N_2H_6 groups and NO_3 groups for the chlorine atoms.

The length of the edge of the unit cube containing four molecules, as deduced from the powder measurements (*1922*, 92) is $a_0 = 8.11$A°.

Strontium Nitrate, $Sr(NO_3)_2$.—Crystals of strontium nitrate are crystallographically isomorphous with those of barium nitrate. Powder photographs (*1922*, 92) and Laue photographic data (*1917*, 16) (not reported in detail) are also similar to those from $Ba(NO_3)_2$ and lead by the process just outlined to the same type of structure [4b; 8h; Ti−6, 24]. In this case, likewise, the powder data have been used to propose values for the four variable parameters. The length of the edge of the unit cube is given as $a_0 = 7.81$A° (*1922*, 92).

Calcium Nitrate, $Ca(NO_3)_2$. Powder data (*1922*, 92) from crystalline anhydrous $Ca(NO_3)_2$ resemble those from the other two alkaline earth nitrates and suggest that it has the same crystal structure. The length of the edge of the unit cube containing four molecules is found to be $a_0 = 7.60$A°.

Lead Nitrate, $Pb(NO_3)_2$.—Crystals of lead nitrate have given rise to Laue photographs, not described in detail (*1917*, 16), and powder photographs (*1922*, 92) which are entirely analogous to those from barium nitrate; these data lead in the manner described for the barium salt to the same type of atomic arrangement [4b; 8h; Ti−6, 24]. The extreme weight of the lead atoms makes this case even more unfavorable than the preceding ones for estimations of the positions of the nitrogen and oxygen atoms. The length of the edge of the unit cube is determined to be $a_0 = 7.84$A° (*1922*, 92).

Hydrates and Ammoniates of Nitrates, Chlorates and Bromates

Zinc Bromate Hexahydrate, $Zn(BrO_3)_2 \cdot 6H_2O$ (1922, 105).—Crystals of this salt are optically isotropic when grown by slow evaporation; their symmetry is therefore cubic. A reflection spectrum from a (111) face combined with the known density shows that $m/n^3 = 4$. There is no evidence from any source that m should be greater than four. From the hemihedry of the Laue photographs it is clear that the symmetry of atomic arrangement is either T or Ti. The data from these photographs are analogous to, but much richer and more conclusive than those from $Ba(NO_3)_2$. The same course of reasoning used for that crystal leads to a choice of Ti−6 as the corresponding space group and to the following modification of the "barium nitrate structure":

Zinc atoms: [4b] 000; $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$ (replacing barium atoms),
Bromine atoms: [8h] (replacing nitrogen atoms),
Bromate oxygen atoms: The 24 generally equivalent positions of [Ti−6, 24],

Water oxygen atoms: [Ti−6, 24], with different values of x, y and z,

Hydrogen atoms: If the hydrogen atoms were to occupy positions agreeing with the crystal symmetry they also would fill two sets of equivalent positions of [Ti−6, 24].

If atomic arrangements which place all of the atoms (except those of the water groups) along the body diagonal with the formation of bromate groups like O–Br–O–O or Br–O–O–O are excluded as not chemically acceptable, this atomic arrangement is the only one possible. Any values which might be assigned to the seven variable parameters of this structure would not be significant.

It should be noted that all six of the water groups in this crystal are equivalent and related in exactly the same manner to each zinc atom. Though of course the impossibility of finding the exact atomic positions prevents a complete experimental proof, it is probable that this structure for $Zn(BrO_3)_2 \cdot 6H_2O$ is, like $Ba(NO_3)_2$, a calcium fluoride arrangement (Figure 171) with (BrO_3) groups in the approximate positions of the fluorine atoms and with $[Zn,6H_2O]$ groups introduced in place of calcium atoms.

The length of the edge of the unit cube containing four molecules is found to be $a_0 = 10.31A°$.

Nickel Nitrate Hexammoniate, $Ni(NO_3)_2 \cdot 6NH_3$ (1922, 109).—This crystalline compound is the same one which has often been described as $Ni(NO_3)_2 \cdot 4NH_3 \cdot 2H_2O$. It is optically isotropic and consequently possessed of cubic symmetry. Spectrum photographs from a (111) face combined with the density of this salt prove that $m/n^3 = 4$; none of the data from these or Laue photographs gives reason for believing that m is greater than four. From this fact and the similarity between the chemical compositions of $Ni(NO_3)_2 \cdot 6NH_3$ and $Zn(BrO_3)_2 \cdot 6H_2O$ it might be expected that the two would exhibit the same type of atomic arrangement. Nevertheless the Laue photographs showed no observable hemihedry and only reflections with all odd indices were found in the first order region. These are the experimental characteristics of photographs from $NiCl_2 \cdot 6NH_3$ rather than $Zn(BrO_3)_2 \cdot 6H_2O$ and they seem to show that $Ni(NO_3)_2 \cdot 6NH_3$ is built upon a face centered rather than a simple cubic lattice. If this conclusion were accepted a course of argument similar to that used for $NiCl_2 \cdot 6NH_3$ (see page 334) would lead to the latter type of structure. In such an arrangement the nitrate oxygen atoms would have the coördinate positions of [24a] or [24c]; in either case the nitrate group would be destroyed. This result appeared so improbable from a chemical standpoint that an effort was made to see whether a more acceptable structure based upon a simple cubic lattice but approaching a face centered one

could be found. Such an arrangement, developed from Ti−6, is as follows:

Nickel atoms: [4b] 000; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$,

Nitrate nitrogen atoms: [8h], if u_N is near $\frac{1}{4}$,

Ammonia nitrogen atoms: The 24 generally equivalent positions of [Ti−6, 24], with x_N, y_N and z_N close to v_N, 0 and 0 respectively.

Oxygen atoms: [Ti−6, 24], with x_O, y_O and z_O near to $\frac{1}{4}$, $\frac{1}{4}$, and v_O.

Hydrogen atoms: As usual the positions of the hydrogen atoms are indeterminable.

Trial with the usual intensity expressions indicates that v_N and v_O can vary considerably from $\frac{1}{4}$ and 0 before conflict with the data is observable. It can also be shown that no other pyritohedral structure and apparently no holohedral grouping developed from a simple cubic lattice will fit the observations. This atomic arrangement is then a possible one for $Ni(NO_3)_2 \cdot 6NH_3$. Besides preserving the nitrate group it has that degree of probability which arises from its similarity to the arrangement in the better established alkaline earth nitrates and $Zn(BrO_3)_2 \cdot 6H_2O$.

It differs from the structure for $NiCl_2 \cdot 6NH_3$ (Figure 184) in two respects: the nitrate groups in replacing the chlorine atoms will not be situated at the centers of the small cubes having the volume of one eighth of the unit; and the ammonia groups around the nickel atoms of $Ni(NO_3)_2 \cdot 6NH_3$ need not lie on the coördinate axes passing through these atoms.

The unit cube containing four molecules is found to have a length of edge: $a_0 = 10.96$A°. This study of structure illustrates some of the pitfalls that would be encountered in a purely routine interpretation of the usual diffraction data.

Carbonates

Calcite, $CaCO_3$ (1914, 12; 1915, 1; 1919, 32; 1920, 63; 1923, 63).— The calcite modification of $CaCO_3$ is one of the most extensively studied of all crystals. Two sets of spectrometer measurements and two separate studies using Laue photographs have been recorded. Crystals of calcite, like those of sodium nitrate, are supposed to have the symmetry of the rhombohedral point group 3Di; they also possess practically the same angle between rhombohedral axes: $\alpha_0 = 101° 55'$. The diffraction effects from these two crystals likewise are of exactly the same character and lead by the reasoning outlined for sodium nitrate to the same type of probable structure, with calcium atoms replacing sodium atoms and carbon entering in place of nitrogen (Figure 189).

There is, however, a disagreement in the values that have been assigned to u, the parameter defining the positions of the oxygen atoms. Making use of the usual "laws" of scattering, the original spectrometer observations (*1914*, 12) led to $u_O = 0.30$; more recent and accurate ones (*1915*, 1) are said to give $u_O = 0.25$. The same higher parameter value ($u_O = 0.30$) has been chosen as a result of a similar quantitative application of the scattering "laws" to Laue data (*1919*, 32). The other study with Laue photographs (*1920*, 63) has made use merely of the presence or absence of first order reflections with either all odd or two even and one odd indices. Such reflections are due only to oxygen atoms and therefore do not involve any assumption concerning the relative scattering powers of different kinds of atoms. Furthermore in employing only the presence or absence of reflections merely the most qualitative use is made of the postulate of the decline of intensity with spacing. For these reasons this last determination of oxygen positions is open to less question on theoretical grounds. Its results agree with the more exact spectrometric observations in placing u_O close to 0.25. Most of the reflections fitted about equally well two regions, one about 0.25, the other around 0.30; but a few data were found which excluded the upper region. It is of interest to note that calculations (*1920*, 21a) of intensities based upon quantitative use of the "laws" of scattering show conflicts with *both* regions.

A choice between possible arrangements [r] and [r'] (see page 348) is most conveniently made from the relative intensities of the spectrometer reflections from the basal plane (111). In eliminating [r'] they result in the following probably correct arrangement for the atoms in calcite:

[r] Carbon atoms: 000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$,
Calcium " $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{3}{4}\frac{3}{4}\frac{3}{4}$,
Oxygen " $uu0$; $u0u$; $0uu$; $\frac{1}{2} - u$, $u + \frac{1}{2}$, $\frac{1}{2}$; $u + \frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2} - u$; $\frac{1}{2}$, $\frac{1}{2} - u$, $u + \frac{1}{2}$, where the most probable value for u is very close to 0.25.

The spacing between physically like atomic planes parallel to the cleavage face [(100) according to the crystallographic axes] is one of the two fundamental wave length standards. It is commonly taken [1] to be: $d_{100}/n = 3.028$A°. The length of the edge of the unit rhombohedron (Figure 189) containing two molecules is then a_2 (Figure 188) = 6.360A°; [2] the angle between its axes is $\alpha_2 = 46° 6'$. The construction cell having the shape of the cleavage rhombohedron and containing four chemical molecules is shown in Figure 190; as stated during the discussion of

[1] See, for instance, W. Duane, Bull. Nat. Research Council I, No. 6 (1920).
[2] In one discussion (*1920*, 63) the absolute dimensions of the unit cell were incorrectly stated for calcite, and also for the manganese and ferrous carbonates.

sodium nitrate this illustration brings out more clearly the fact that the calcite structure can be pictured as a sodium chloride grouping (Figure 167) of calcium atoms and carbonate groups which has been somewhat compressed along a three-fold axis.

Rhodochrosite, $MnCO_3$ (1914, 12; 1920, 63).—Crystals of $MnCO_3$ have symmetry properties which are very similar to those of calcite. Spectrometer (*1914*, 12), spectrographic and Laue photographic (*1920*, 63) observations lead by a procedure identical with that outlined for sodium nitrate and calcite to the same type of probable atomic arrangement (Figure 189). The early spectrometer measurements (*1914*, 12) indicated that the oxygen parameter u_O was greater than 0.30; but the Laue data (*1920*, 63) treated in the same way that was used for one investigation of calcite give $u_O = 0.27$. This second value seems to be the more probable. The length of the edge of the unit rhombohedron containing two molecules (Figure 189) is a_2 (Figure 188) = 5.836A°; the angle between its axes is $\alpha_2 = 47° 45'$.

Siderite, $FeCO_3$ (1914, 12; 1920, 63).—Crystals of ferrous carbonate are crystallographically isomorphous with those of $MnCO_3$. The Laue photographs (*1920*, 63) to which they have given rise, though much poorer than those from $MnCO_3$, are scarcely distinguishable from them. These photographs and the spectrum photographs that have been prepared yield the type of atomic arrangement displayed by these other carbonates [r]. The similarity in the Laue data from these two crystals is such that u_O probably is near to 0.27.

The length of the edge of the unit rhombohedron containing two molecules (Figure 189) is found to be a_2 (Figure 188) = 5.822A°; the angle between its axes is, like that of manganese carbonate, $\alpha_2 = 47° 45'$.

Dolomite, $CaMg(CO_3)_2$.—The question of whether dolomite is a solid

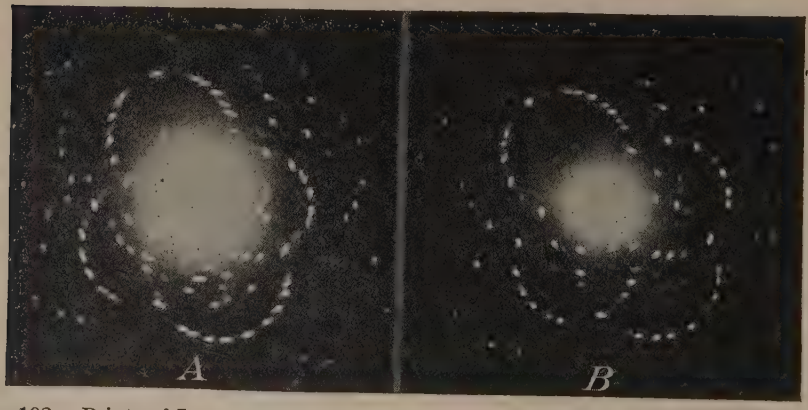


FIG. 192.—Prints of Laue photographs of calcite (A) and dolomite (B) taken with the incident X-rays nearly normal to cleavage faces The lower symmetry of the dolomite pattern is evident.

solution of calcium and magnesium carbonates or a definite compound of the two has been widely discussed. Laue photographs [1] (Figure 192) show a hemihedry which, in giving a symmetry to this crystal lower than that of either magnesium carbonate or calcite, proves it to be a distinct crystalline species. Except in the characteristics introduced by this hemihedry, the Laue data closely resemble those of calcite and when taken in connection with the spectrum photographs they point to the same kind of a unit rhombohedron. This unit contains one molecule of $CaMg(CO_3)_2$. The Laue photographs show that the symmetry of atomic arrangement is either 3C or 3Ci; there is no crystallographic evidence for the former. Assuming the symmetry to be that of 3Ci and admitting the existence of CO_3 groups, the atomic arrangement within the unit (Figure 193) must then be:

[s] Calcium atom: 000,
Magnesium atom: $\frac{1}{2}\frac{1}{2}\frac{1}{2}$,
Carbon atoms: uuu; $\bar{u}\bar{u}\bar{u}$,
Oxygen atoms: xyz; zxy; yzx; $\bar{x}\bar{y}\bar{z}$; $\bar{z}\bar{x}\bar{y}$; $\bar{y}\bar{z}\bar{x}$.

No attempt has been made to assign values to these four variable parameters. Nevertheless this structure can undoubtedly be looked upon as like that of calcite with half of the calcium atoms replaced by magnesium atoms; the carbonate groups, however, need not have the same shape as in calcite, nor will they be related in exactly the same way to the calcium and to the magnesium atoms of $CaMg(CO_3)_2$.

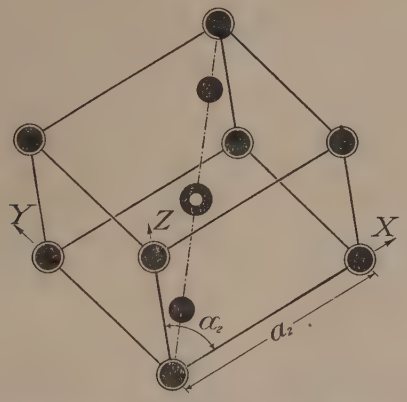


FIG. 193.—The unit rhombohedron of the dolomite arrangement [s] showing the positions of the calcium (ringed circles), magnesium (annulus) and carbon (black circles) atoms. The position of the carbon atoms on the body diagonal of this unit is not determined.

[1] Except for a single spectrometer measurement upon a (111) face (*1914*, 12), data by H. E. Merwin and the writer (as yet unpublished) form the basis for these results.

The length of the edge of the unit rhombohedron (Figure 193) containing one molecule has been found to be a_2 (Figure 188) = 6.022A°; the angle between its axes is $\alpha_2 = 47° 7'$.

A study has also been made of an iron-bearing dolomite which has the approximate composition: 70% $CaMg(CO_3)_2$·30% $CaFe(CO_3)_2$. Laue photographs give data entirely analogous to those from pure dolomite and yield the same probable atomic arrangement [s]. This mineral can thus be considered as a dolomite in which about 30% of the magnesium atoms are replaced through solid solution by atoms of ferrous iron. It is remarkable that the absolute dimensions of the unit rhombohedron of this crystal are the same, within 0.2%, as those of the iron-free dolomite.

Silicates

Olivine, ($Mg, Fe)_2SiO_4$ (*1921, 12*).—Spectrum and Laue photographic data have been obtained from this orthorhombic crystal. In the specimen studied the ratio of magnesium to ferrous iron was about six to one. Very voluminous Laue data were recorded but little use was made of them in the subsequent study of atomic arrangement. It was thought that secondary reflection spectra establish the probable space group as $_2$Di−16. A unit corresponding to the usually chosen axial ratio was used but no effort seems to have been made to show that it agrees with all attainable experimental data. In view of this apparent failure to determine at least the simplest possible unit cell, little significance can be attached to the results of this study.

Garnet, (*1917, 15*).—Crystals of garnet have the composition $R_3''R_2'''(SiO_4)_3$, where R″ and R‴ are various di- and tri-valent metallic elements. Spectrum and Laue photographic measurements have been made upon an iron-manganese aluminum garnet but the experimental data have never been published in detail. The spectrum photographs are said to show that $m/n^3 = 1$; the Laue photographs indicate that m = 8 and that the corresponding space group is Oi−10. If this is true then the atomic arrangement must be one of the following (*1922,* 111):

R‴ atoms: [16h] or [16i],
R″ " [24v] or [24w],
Si " [24w] or [24v],
O " The generally equivalent positions of Oi−10 [Oi−10, 96], two sets of [48m] or [48n], or three sets of [32f].

The available data do not permit of a decision between these possible groupings. A more thorough knowledge of this structure would undoubtedly throw valuable light upon the nature of silicates and to this end a more extensive study of the garnets is to be desired.

The length of the edge of the unit cube containing eight molecules of $R_3''Al_2(SiO_4)_3$, where R'' is about two thirds ferrous iron and one third manganese, is given as $a_0 = 11.40A°$.

Sulfates, Molybdates, Tungstates, etc.

Alkali Sulfates.—Spectrometer observations (*1916*, 21) have been carried out upon crystals of the isomorphous series of the sulfates of potassium, ammonium, rubidium and cesium. These measurements were undertaken primarily to test the hypothesis of valency-volume. They and many other diffraction data conclusively discredit this hypothesis. The spectrometer data in themselves are inadequate for the determination of atomic arrangement in these orthorhombic crystals and have not in fact been seriously applied to this purpose.

Powder photographs (*1921*, 84) have been prepared from ammonium and potassium sulfates and from a solid solution of the two. No numerical data, however, have been published.

Silver Molybdate, Ag_2MoO_4 (*1922, 110*).—Crystals of silver molybdate are isotropic and therefore cubic. Spectrum and Laue photographs yield data which are similar to those from $K_2Zn(CN)_4$ and lead by the steps outlined for this cyanide to the same type of structure. The manner of atomic arrangement for this crystal must therefore be (*1922*, 111):

Molybdenum atoms:		[8f],
Silver	"	[16c],
Oxygen	"	[32b].

The relatively great scattering powers of the silver and molybdenum atoms prevent an accurate placing of the oxygen atoms; it is nevertheless possible to show that u_o can scarcely lie outside of the limits $0.34 < u < 0.40$ and that it probably is close to 0.37.

The length of the edge of the unit cube containing eight molecules (Figure 186) is found to be $a_0 = 9.26A°$.

Scheelite, $CaWO_4$ and Wulfenite, $PbMoO_4$ (*1920, 20*).—Spectrometer data have been obtained from various faces of these two tetragonal crystals. Such measurements and their treatment do not seem sufficient to determine the atomic arrangement in these crystals with any degree of certainty. Reproductions of unanalyzed Laue photographs have also been published (*1916*, 14).

Alums (*1914, 38; 1918, 21, 27; 1923, 96*).—The formula of these cubic crystals is $R'R'''(XO_4)_2 \cdot 12H_2O$, where R' may be potassium, ammonium, rubidium, cesium or thallium; R''' is one of such trivalent atoms as aluminum, chromium, iron, gallium, etc., and X is either sulfur or selenium.

Spectrometric observations (*1918*, 27) have been carried out upon $KAl(SO_4)_2 \cdot 12H_2O$, $NH_4Al(SO_4)_2 \cdot 12H_2O$, $NH_4Fe(SO_4)_2 \cdot 12H_2O$ and $KCr(SO_4)_2 \cdot 12H_2O$. Laue and spectrum photographic studies (*1923*, 96) have also been made upon the first two. The reflections from single faces show that $m/n^3 = 4$; there are no evidences that m is greater than four. The Laue photographs exhibit a marked hemihedry so that the symmetry of atomic arrangement must be that of either T or Ti. From the presence of first order reflections with all odd, two odd and one even and two even and one odd indices it is clear that the fundamental lattice is the simple cubic Γ_c. A distinction between the possible space groups can be made from a study of odd order reflections with one index zero. It is found that the requirements of the space group Ti−6 are completely met. Reference to the results of the theory of space groups (*1922*, 111) indicates immediately that the atoms in the alums must occupy the following positions:

R′ atoms: [4b], 000; $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$,
R‴ " [4c], $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $00\frac{1}{2}$; $0\frac{1}{2}0$; $\frac{1}{2}00$,
X " [8h],

"Sulfate" oxygen atoms: Eight atoms at [8h], with $u_O \neq u_X$, and 24 atoms in the generally equivalent positions of [Ti−6, 24].

Hydrate oxygen atoms: Two sets of atoms in the positions [Ti−6, 24].

Water hydrogen atoms: If these hydrogen atoms were to occupy positions which conform to the symmetry of the crystal as a whole they would lie in four sets of [Ti−6, 24].

Inasmuch as there are 11 variable parameters, excluding those governing the hydrogen positions, no attempt can profitably be made to define the coördinate values for any except the metal atoms. The arrangement of these atoms within the unit cube is shown in Figure 194.

It will be noticed that three of the oxygen atoms in the sulfate group are geometrically alike but different from the fourth and that the water oxygen atoms fall into two groups of six each. These groups of water molecules are most readily imagined as arranged one about each metal atom.

The lengths of the edges of the unit cubes containing four molecules have been found to be (*1918*, 27):

Crystal	a_0
$KAl(SO_4)_2 \cdot 12H_2O$	12.08A°
$NH_4Al(SO_4)_2 \cdot 12H_2O$	12.00
$NH_4Fe(SO_4)_2 \cdot 12H_2O$	12.14
$KCr(SO_4)_2 \cdot 12H_2O$	11.93

The attempt to find coördinates to express the manner of arrangement of the ammonium hydrogen atoms in the ammonium alums introduces an important difficulty (*1923*, 96). The only way of placing 16 hydrogen

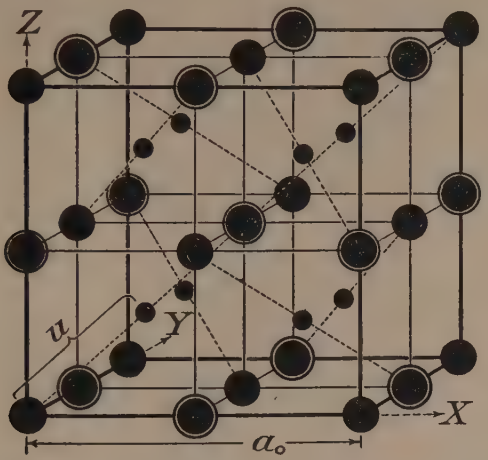


FIG. 194.—The unit cube of the atomic arrangement in crystals of the alums. The alkali metal atoms are represented by large black circles, the trivalent atoms by ringed circles and the sulfur (or selenium) atoms by small black circles. The parameter u stating the positions of these sulfur atoms is not determined; neither can the location of the oxygen atoms be shown. As long as the value of u is not defined an interchange of the positions of the uni- and tri-valent atoms would not be significant.

atoms within the unit cube divides them into two sets in positions of [8h]. The resulting ammonium groups (Figure 195), in which the hydrogen atoms are no longer directly associated with a central nitrogen atom, are chemically improbable. The simplest escape from the difficulty thus introduced lies in the assumption that the ammonium group functions crystallographically as well as chemically as a single entity and that its hydrogen atoms need not therefore occupy positions which conform to

FIG. 195.—If their atoms occupy positions which conform to the symmetry of the crystal as a whole, the ammonium groups of the ammonium alums must have the form shown in this figure.

the demands of the crystal symmetry. This hypothesis probably cannot be directly tested either optically or with X-rays because it is unlikely that the hydrogen nuclei are centers of electron motions. The greater simplicity that results from an application of this assumption to the

structures of the ammonium halides has been suggested (page 210); further experimentation will show whether its use is required for other crystals.

The apparently erroneous spectrometer measurements (*1918*, 27) upon these alums and the probable cause of the spurious reflections there encountered have already been mentioned (see page 172).

Borates, Aluminates, Ferrites, etc.

Tourmaline (*1921*, *63*).—Many Laue and spectrum photographic data have been published for a tourmaline of unknown chemical composition. The spectrum measurements are thought to show that the underlying lattice is hexagonal. They have also been used to suggest both a unit cell and possible corresponding space groups. The mass associated with the unit could not be given (in the absence of a knowledge of the composition) and no atomic arrangement can be even proposed.

Spinel, $MgAl_2O_4$.—Spectrometer (*1915*, 2), spectrographic and Laue photographic (*1915*, 17) observations have been made upon this cubic crystal. These data are similar to the measurements from crystals of $K_2Zn(CN)_4$ and by the reasoning outlined for such crystals will yield the same type of structure. In the unit cell (Figure 186), which hence contains eight molecules of $MgAl_2O_4$, the atoms occupy the following positions:

Magnesium atoms:		[8f],
Aluminum	"	[16c],
Oxygen	"	[32b].

The parameter u for oxygen is found to be close to 0.37 (as for the rest of the crystals having this structure). No X-ray determination of the length of the edge of the unit cube has been carried out.

Magnetite, Fe_3O_4.—Powder photographs (*1922*, 43), as well as Laue photographs (*1915*, 17) and spectrum measurements (*1915*, 2), are available for Fe_3O_4. The data are similar to those from spinel and $K_2Zn(CN)_4$ and lead to the same type of structure. The atomic arrangement then is given by (Figure 186):

Ferrous iron atoms:		[8f],
Ferric iron	"	[16c],
Oxygen	"	[32b].

The parameter u for oxygen is close to $\frac{3}{8}$. The length of the edge of the unit cube containing eight molecules is stated (*1915*, 2) to be $a_0 = 8.30$A°.

Other Members of the Spinel Group.—Spectrometer measurements (*1915*, 2) from a single face of gahnite ($ZnAl_2O_4$) are similar to those from magnetite. Powder photographs (*1922*, 43) from Co_3O_4 are similar to

those from magnetite. No determination of the length of edge of the unit cube has been made in either of these cases.

Chalcopyrite, $FeCuS_2$.—Spectrometer (*1917*, 2) and Laue photographic (*1923*, 43) measurements have been made from this tetragonal crystal. They show that a unit cell containing two molecules is possible if it has the following dimensions:

$a_0 = 5.23A°$, $c_0 = 5.15A°$, corresponding to the usually chosen axial ratio $a : c = 1 : 0.985$. Without a discussion of the other arrangements which are in accord with the observed symmetry (of which there are many) it has been considered (*1923*, 43) that the following is in agreement with the experimental data (see space group 4d–5):

[t] Iron atoms: $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$,
Copper atoms: 000; $\frac{1}{2}\frac{1}{2}0$,
Sulfur atoms: $\frac{1}{4}\frac{1}{4}u$; $\frac{1}{4}\frac{3}{4}\bar{u}$; $\frac{3}{4}\frac{1}{4}\bar{u}$; $\frac{3}{4}\frac{3}{4}u$.

The spectrometer data make $u_S = \frac{1}{4}$; from the Laue measurements u_S is assumed to be close to 0.21. Inasmuch as quantitative use was made of the "laws" of scattering (the atomic weight enters into the second estimation), these values of u_S cannot be taken as accurate in either case. The unit cell of this possibly correct structure for chalcopyrite is shown in Figure 196. As the figure shows this arrangement can be pictured as a

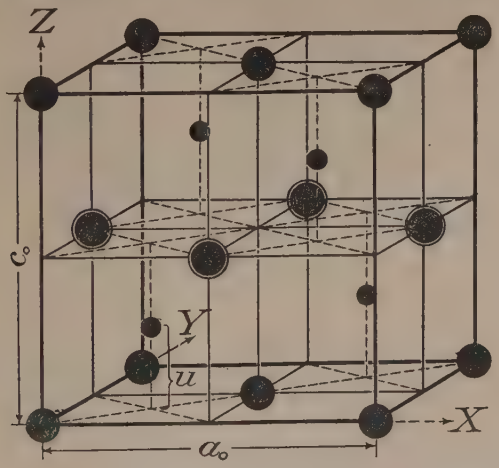


FIG. 196.—The unit cell of the chalcopyrite structure [t]. According to the description in the text the copper atoms are represented by large black circles, the iron atoms by ringed circles and the sulfur atoms by small black circles.

cubic "zinc sulfide grouping" (Figure 174) slightly distorted by compression along the c-axis and having half of the zinc atoms replaced by iron, the other half by copper atoms.

Phosphates

Xenotime, YPO_4.—Spectrometer measurements (*1916*, 32; *1917*, 25) were made upon YPO_4 at the same time that similar observations were carried out upon the related tetragonal crystals rutile, zircon, etc. As is true for these other crystals the data upon YPO_4 and their treatment are not sufficient for the determination of the probably correct atomic arrangement.

Organic Compounds

Sodium Hydrogen Acetate, $NaH(C_2H_3O_2)_2$ (1922, 106).—Spectrum and Laue photographs from this isotropic crystal have been studied. The former yield $m/n^3 = 3$. From the Laue photographs and measurements of secondary spectra it appears that 24 rather than three molecules are contained within the unit cube. The Laue photographs exhibit the hemihedry characteristic of either tetartohedral or pyritohedral crystals. The only first order reflections found from this larger unit have two odd and one even indices; this indicates that the fundamental lattice is the body centered Γ_c''. Of the four space groups T−3, T−5, Ti−5 and Ti−7 which thus remain as possibilities, Ti−7 is characterized by the absence of odd orders of [0kl], where k and l are both odd. Since none of these reflections was found though some were in good positions to reflect, it is possible that the corresponding space group is Ti−7. The atomic arrangement would in any case be so complicated that it could not be established at present. The length of the edge of the unit cube containing 24 molecules of $NaH(C_2H_3O_2)_2$ is found to be $a_0 = 15.98A°$.

It is a matter of some surprise that this crystal should prove to have so complicated a structure, especially in view of the fact that what would be considered a chemically plausible arrangement can be developed from a three-molecule unit. The experimental data were, however, very full and perfectly definite and the crystals studied gave every evidence of being single individuals.

Hexamethylene Tetramine, $C_6H_{12}N_4$ (1923, 38).—The structure of this cubic crystal has been investigated with the aid of spectrum and Laue photographs. The former, combined with the density, yield $m/n^3 = 2$; there is no evidence suggesting that more than two molecules are contained within the unit cube. The Laue photographs show complete cubic symmetry so that the symmetry of atomic arrangement is that of Te, O or Oi. The presence of only reflections with two odd and one even indices in the first order region indicates that the fundamental lattice is body centered. Of the body-centered space groups giving holohedral diffraction patterns, Te−6 and Oi−10 are excluded (see Table III, Chapter

VII) by the presence of such first order reflections as 433(1) or 510(1). Similarly the second order reflection from (100) eliminates O−8. In general the three remaining groups Te−3, O−5 and Oi−9 are indistinguishable. Arrangements developed from the last two destroy the physical existence of molecules of $C_6H_{12}N_4$; a grouping arising from Te−3 leaves the chemical molecule intact. If it is assumed that such molecules actually are present in these crystals then the atomic arrangement in the unit cell of $C_6H_{12}N_4$ must be as follows:

Nitrogen atoms: [8a] (see *1922*, 111),
Carbon " [12a].

Neglecting values of u_C which bring carbon atoms closer together than 1 A° and assuming that the scattering powers of carbon and nitrogen atoms are proportional to six and seven respectively, parameters which qualitatively agree with the spectrum and Laue data have been found to be: $u_N = 0.12$, $u_C = 0.235$. The accuracy of these variable parameter assignments depends upon the correctness of the choice of scattering powers.

This arrangement [8a, 12a] happens also to be a special case of the simple cubic space group Te−4. The published determination of structure does not eliminate experimentally the non-molecular groupings arising from Te−3, O−5 and Oi−9. The length of the edge of the unit cube

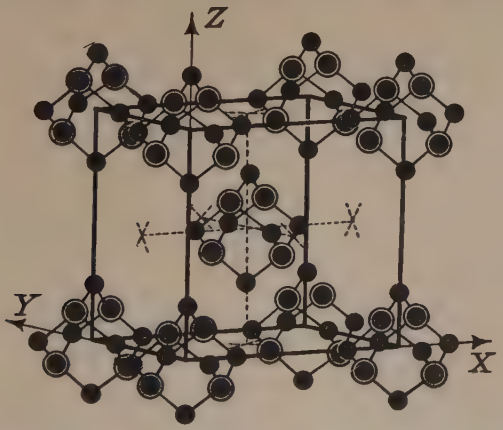


FIG. 197.—The distribution of the molecules of hexamethylene tetramine within its unit cube. The carbon atoms are shown as black circles, the nitrogen atoms as ringed circles.

containing two molecules is found to be $a_0 = 7.02$A°. The distribution of these molecules is shown in Figure 197. If the hydrogen atoms have positions which conform to the crystal symmetry and if the space group

is Te−3, rather than Te−4, they will have the arrangement [24g]. Such a grouping surrounds each carbon atom with two nitrogen and two hydrogen atoms located at the corners of a tetrahedron (Figure 198).

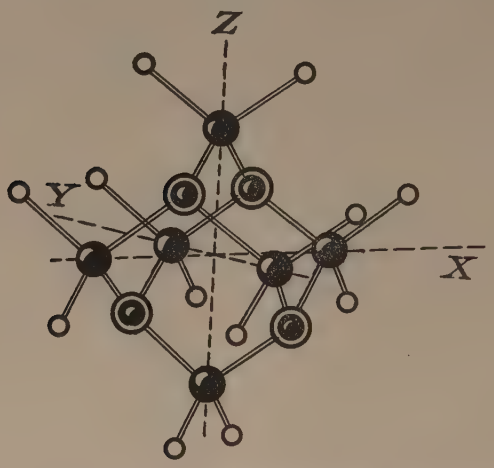


FIG. 198.—The shape of the molecule of hexamethylene tetramine as determined by a study of its crystal structure. Possible positions for the hydrogen atoms are given by the open circles. As in the preceding figure carbon atoms are represented by black, nitrogen atoms by ringed circles.

A surprising and disconcerting observation made upon these photographs is the absence of any reflections in wave lengths below 0.30A° when the original beam contained effective wave lengths down to 0.23A°. The experimental observation of these low wave length limits in Laue photographs forms probably the best means of selecting between possible unit cells in crystals with less than cubic symmetry. If $C_6H_{12}N_4$ had formed crystals with other than cubic symmetry such data as these would almost certainly have led to a choice of an incorrect unit. With this fact in mind it is clear that an investigation of the causes of this discrepancy and the development of an experimental technique for its elimination is a necessary prelude to the Laue photographic study of organic and other crystals of low symmetry.

Urea, $CO(NH_2)_2$ (1921, 11; 1923, 60).—Crystals of urea exhibit tetragonal symmetry. Reflection spectrum photographs (*1923*, 60) have been prepared using several simple planes as principal faces and an attempt has been made to deduce the structure of urea from a study of the principal and secondary reflections thus obtained.

From the relative spacings of the first observed reflections from (100), (110) and (111) it has been concluded that the fundamental lattice is the simple tetragonal Γ_t and that the corresponding unit prism has the dimen-

sions $a_0 = 5.63A°$, $c_0 = 4.70A°$ and contains two molecules of $CO(NH_2)_2$. It is not entirely clear how unique is a determination of true unit cell based upon these data. Assuming its correctness the observed reflections can be shown to meet the requirements (*1919*, 24) of only the space group 4d−3. In order to preserve molecules of urea the carbon and oxygen atoms presumably will occupy the two equivalent positions $0\frac{1}{2}u$; $\frac{1}{2}0\bar{u}$ (with $u_C \neq u_O$) and it is found that all four of the nitrogen atoms must be equivalent, probably with the grouping (*1922*, 111):

$$u, \tfrac{1}{2} - u, v; \tfrac{1}{2} - u, \bar{u}, \bar{v}; \bar{u}, u + \tfrac{1}{2}, v; u + \tfrac{1}{2}, u, \bar{v}.$$

No determination of the variable parameters can be made. It will be noticed that if this structure is correct, the carbon, oxygen and the two nitrogen atoms of a urea molecule all lie in one plane.

Pentaerythrite, $C(CH_2OH)_4$ (*1921, 11; 1923, 60a*).—Crystals of pentaerythrite have tetragonal symmetry. Using methods of experimentation and analysis identical with those employed for urea it is concluded (*1923*, 60a) that the unit tetragonal prism contains two molecules of $C(CH_2OH)_4$ and has the dimensions $a_0 = 6.16A°$, $c_0 = 8.76A°$. Assuming, in accordance with crystallographic indications, that the symmetry is expressed by the point group 4e, it has been found that, for this unit cell, the space group 4e − 9 is the only one (*1919*, 24) which agrees with the experimental data. These data do not, however, seem capable of selecting the correct arrangement from among the several which can be deduced from this space group.

Other Organic Crystals.—Diffraction data, for the most part from either spectrometer measurements or powder photographs, have been collected from a number of other organic substances. In the foregoing it has been pointed out that neither spectrometer data obtained in the usual fashion nor powder photographs alone are necessarily trustworthy guides to crystal structure. Furthermore the unit cells used in these investigations are not chosen after the consideration and elimination of other geometrically possible ones. For these reasons alone a detailed treatment of these data and of the extensive discussions of structure which accompany some of them would not be justified.

Among the crystals studied in this manner may be mentioned: Benzene (*1923*, 25); naphthalene (*1921*, 11, 19); anthracene (*1921*, 11; *1923*, 17); resorcinol (*1921*, 11; *1922*, 18); hydrochinone (*1922*, 11; *1922*, 18); tartaric acid (*1921*, 11; *1923*, 3); racemic acid (*1923*, 4); benzoic acid (*1922*, 18); dibenzyl (*1923*, 12a); stilbene (*1923*, 12a); benzil (*1923*, 12a); triphenylcarbinol (*1923*, 12a); mannite (*1923*, 12a); cane sugar (*1923*, 12a); indigo (*1921*, 11); succinic acid (*1921*, 11); quinone (*1921*, 11); phenanthrene (*1921*, 11); phthalic acid (*1921*, 11); phthalic anhydride (*1921*, 11);

cinnamic acid (*1921*, 11); hydrocinnamic acid (*1921*, 11); azobenzene (*1921*, 11); hydrazobenzene (*1921*, 11); lithium oxalate (*1921*, 11); basic beryllium acetate (*1923*, 19); maleic acid (*1921*, 11); succinic anhydride (*1921*, 11); maleic anhydride (*1921*, 11); α-methyl glycoside (*1921*, 11); acetylene dicarboxylic acid (*1921*, 11); α- and β-naphthol (*1921*, 19); acenaphthene (*1921*, 19); lithium formate, proprianate, valerate, heptylate, nonylate, undecylate, acetate, butyrate, caprylate, laureate, stearate, isobutyrate, isovalerate, trimethylacetate, crotonate, oleate (*1921*, 11a); lauric, myristic, palmitic, stearic, elaidic acids (*1921*, 11a); $\alpha\alpha'$ distearin (*1921*, 11a). Data upon triphenylmethane (*1923*, 12a, 60b, 12b) are conflicting.

Chapter XIV. Incomplete Crystalline and Non-crystalline Diffraction Phenomena

The preceding chapters have been devoted to a consideration of the diffraction effects obtained through the action of X-rays upon the indefinitely extended regular grouping of atoms which constitutes a crystal. It is also essential to investigate the phenomena arising from the scattering of X-rays by the atoms in substances possessing less than this complete regularity of atomic arrangement.

Diffraction effects different from those thus far described are encountered (1) from crystals in which the regularity of atomic arrangement is for some reason incomplete or imperfectly maintained and (2) from matter in other than the crystalline state of aggregation.

Compared with the diffraction phenomena from complete crystals, little is known of these effects; practically no exacting work has yet been carried out upon any of them.

Most of the phenomena to be described are best obtained using monochromatic radiation according to the powder technique.

Diffraction Effects from Incomplete and Imperfect Crystals

It has long been known that poorly constructed crystals and crystals which have been subjected to deformations give diffraction effects which are unlike the regular "reflections" from atomic planes. The nature of some of these has been briefly mentioned in another place (see page 146). In sufficiently well constructed crystals there has never been any difficulty in distinguishing these effects from the regular reflections. Partly for this reason they have not yet been subjected to any detailed study and no adequate theoretical description of them has been offered.

Amorphous or General Scattering from Crystalline Substances.—A detailed theoretical treatment (*1913*, 19, 21) has indicated that increased amplitudes of atomic vibration leave the relative positions of X-ray diffraction effects unaltered but decrease their intensities, the decrease being greater the larger the angle through which the X-ray beam has been bent. These conclusions have been confirmed in a qualitative fashion by spectrometric observations upon sodium chloride (*1914*, 5) and a few other

crystals (*1922*, 7) at an elevated temperature and by Laue photographs of sodium chloride (*1914*, 32) taken at room temperature and at about 300°C.

Only a general blackening has been found on a powder photograph of metallic potassium (*1917*, 9) at room temperature. At low temperatures (about −150°C) potassium gives a crystalline diffraction (*1922*, 58) but this pattern is completely lost before the sample has warmed to ordinary temperatures. Similarly sodium (*1917*, 9) at room temperature gives only faint lines upon a much blackened field. This has usually been interpreted to mean that potassium, and to a lesser extent sodium, are difficult to crystallize. Potassium thus would be present as an amorphous metal. This explanation conflicts with the sharp melting point found for potassium and with the observation that it can be crystallized in definite octahedrons [1] from the molten state. It seems much more probable that even at room temperature the amplitudes of the thermal vibrations of potassium atoms are great enough to obliterate the crystalline diffraction maxima.

The low melting point of this non-molecular metal and the comparative weakness with which its atoms are bound together, as revealed by numerous mechanical properties, confirm this idea.

From this standpoint the effect of increasing temperature upon the X-ray diffraction pattern from crystals might be pictured in somewhat the following manner: At a sufficiently low temperature (where the specific heat is zero) the atoms will occupy their equilibrium positions and all the energy diffracted by them will be devoted to the production of a crystalline pattern. When increase in temperature has resulted in an appreciable amplitude of atomic vibration, the phase relationships of the scattered X-rays will no longer be completely maintained and there will be a consequent loss in the intensity of crystalline diffraction. It may be anticipated that if this amplitude becomes sufficiently great compared with the wave lengths of the X-rays used, regularities in the phase relationships of the scattered rays may be destroyed. At low temperatures only a few atoms will be possessed of such large amplitudes, but as the crystal becomes hotter the general (or "amorphous") scattering resulting from them may eventually blot out the crystalline effects arising from the diminishing number of low-amplitude atoms. From this point of view the pattern of crystalline potassium, for instance, ought to pass with increasing temperature from that of a good crystal gradually through one of weakened crystalline pattern upon a background of a general blackening to a final complete absence of diffraction lines upon this field of greater "amorphous" scattering. Such a transition has not yet been experimentally established

[1] Long, Quart. J. Chem. Soc. *13*, 122 (1860).

for a single crystal. It also would be a requirement of this hypothesis that the longer the wave lengths used, the higher the temperature at which traces of a crystalline pattern could be detected.

If this explanation of the "amorphous" scattering of crystalline potassium is correct, then its quantitative development ought eventually to supply an experimental method of investigating the amplitudes of atomic vibrations in crystalline solids.

The fact that potassium loses its diffraction pattern at a temperature relatively so remote from its melting point brings forward the question of whether all crystals become incapable of producing crystalline diffraction patterns before melting. An examination of the diffraction of metallic gallium [1] indicates that this is not the case. Gallium gives a pattern, accompanied by only a moderate amount of general scattering, at least to within 1° C of its melting point. Two reasons suggest themselves for this difference in the behavior of metallic potassium and metallic gallium. In the first place there may be no direct connection between the amplitude of atomic vibration and the melting point; it would seem more probable, however, that some relation does exist between them and that one must look for the operation of some modifying influence in the case of gallium. The most obvious factor of this sort is the existence of chemical molecules within the solid. Thus it is possible that the amplitudes of thermal vibration must approach the interatomic distances before melting takes place in crystals which do not contain molecules and within which as a consequence each atom is held to its nearest neighbors by some sort of "primary valency" bondings. Whereas in such non-molecular solids all of an increase in the energy of thermal agitation contributes towards an increase in the atomic amplitudes, in a crystal built of chemical molecules this increment of energy would be distributed. Some of it would be applied to the atomic amplitudes but much might be expected to produce a vibration of the molecule as a whole. Since these molecules are as a rule much heavier than single atoms and since they are held together by relatively weak bonding forces, it is to be expected that neither their amplitudes as a whole nor the amplitudes of the atoms composing them will be nearly so great at their melting points as are the amplitudes of the atoms in non-molecular crystals.

If this point of view is essentially a true one a study of the diffraction patterns of substances at various temperatures below their melting points ought to be capable of furnishing evidence for the existence in crystals of molecular associations of atoms.

A general blackening has also been obtained from metallic crystalline

[1] R. W. G. Wyckoff, J. Wash. Acad. Sci. *14*, 121 (1924).

copper [1] which has been severely polished; it has also been observed that crystalline diffraction is given by faces of native copper crystals only after they have been etched with acid (*1914*, 10). The former observation has been offered as a possible indication of the existence of amorphous metal. It is known that the diffraction patterns obtained from distorted crystals are no longer clear cut but become increasingly diffuse the greater the deformation to which they are subjected. Whether this polishing has succeeded in literally tearing copper crystals apart atom by atom with the formation of a truly amorphous surface layer of metal or whether it has merely strewn the surface with minute deformed crystals of copper, is a question that is not answered by this particular experiment.

X-ray Diffraction Patterns from Crystals of Colloidal Dimensions.—The influence of a very minute size of crystals upon their X-ray diffraction effects can be indicated by having recourse to the reflection analogy. In Figure 69 AO may be imagined to be a beam of X-rays incident upon a series of parallel atomic planes the traces of which are e_1, e_2, e_3, etc. The phase relations existing between the waves reflected by these planes depend of course upon the distance apart of the planes, the wave lengths of the X-rays and the angle θ of incidence. When this angle is such that the path difference of the waves reflected by adjacent planes (such as e_1 and e_2) equals the length of the X-ray wave (or some integral multiple thereof) the reflected waves will reinforce one another and produce a strong diffraction effect. If the incident angle has such a value that these waves are exactly opposite in phase, then they will destroy one another along the direction of reflection. For all other angles, however, the phase relationships of the two rays will lie somewhere between these limits of complete constructive and complete destructive interference. If there is a sufficiently large number of these reflecting planes, as is true for large crystals, then it will always be possible to find reflections from some pair of planes, more or less distant from one another, which are practically opposite in phase. The result from such a large crystal is, as has already been seen, a series of sharp diffraction effects. On the other hand, if the crystalline particle is so small that there are not enough atomic planes to produce this obliteration of reflections for rays of intermediate phase, the diffraction maxima will not be sharp but will become wider and more diffuse the smaller the crystal.

The observed width (*1918*, 24; *1920*, 52) of a spectrum line from very small crystals depends upon other factors than their size. It will be related to the wave length of the diffracted X-rays and the angle of the diffraction as well as in a less intimate fashion to the size of the diffracting

[1] Reported in a lecture by W. Rosenhain; a large amount of scattered radiation from a polished surface of a copper tree has also been observed by the writer.

sample and the width of the spectrograph slits. Since the absolute width of a diffuse line has no precise meaning it has been customary to measure the distance from its center to a point where the intensity is half that at the maximum. A quantitative expression connecting these various factors has been stated for the case of a cubic crystal. This equation has the form

$$B = 2\sqrt{\frac{\log_e 2}{\pi}} \quad \frac{\lambda}{D} \frac{1}{\cos\theta} \quad \ldots\ldots\ldots\ldots (40)$$

where B is the half-intensity width just defined, λ is the wave length of the X-rays, D is the length (in A°) of the edge of the crystalline particle taken as a cube and 2θ is as usual the angle of diffraction.

Such minute crystals would most naturally be sought amongst the chemical precipitates of highly insoluble compounds and in colloidal preparations. As yet little work has been done in investigating the size and nature of either by this method. A few preliminary observations (*1922*, 41) have shown that some metallic sulfide precipitates contain crystals so minute that their diffraction patterns are no longer sharp. Both alpha- and meta-stannic acids are composed of minute crystals [1] having the same type of atomic arrangement that is exhibited by the mineral SnO_2 (cassiterite). The diffraction patterns of these two stannic acids differ only in that the lines from the alpha-form are wider than the ones from the other modification. The powder lines of colloidal gold (*1920*, 52) have the same positions as those of a coarsely crystalline precipitate. The same thing holds true for colloidal preparations of metallic silver.

All colloidal preparations do not furnish crystalline diffraction patterns. For instance no diffraction lines were obtained from a silica gel[2] from which most of the water had been removed by freezing. Preliminary results from an aged silica gel seem contradictory—one observation showing the presence of diffraction lines (*1917*, 11), the other yielding none (*1920*, 52). Gelatine (*1920*, 52) also does not give any evidence of crystallinity. Rice starch (*1920*, 52) and cellulose (*1920*, 51) from different sources, on the other hand, show well-defined crystalline patterns.

The size of particles of colloidal gold (*1920*, 52) has been estimated with the aid of expression (40). The gold preparations used were in the form of a dry powder, gelatine being the protecting agent. The measurements upon the powder photograph of one of these are recorded in Table I. If the values of B contained in the fourth column of this table are plotted against the corresponding values of $1/\cos\theta$, the straight line of Figure 199 is obtained. It will be noticed that this line does not pass through the

[1] E. W. Posnjak, unpublished data from this laboratory.
[2] E. W. Posnjak, unpublished observations.

TABLE I. DATA FROM A POWDER PHOTOGRAPH OF A PREPARATION OF COLLOIDAL GOLD (*1922*, 52)

INDICES OF LINE	θ	$1/\cos\theta$	B(in mm.)
111(1)	19.3°	1.060	1.36
100(2)	22.4	1.082	1.32
110(2)	32.7	1.190	1.30
113(1)	39.15	1.291	1.40
111(2)	41.25	1.333	1.40
100(4)	49.7	1.515	1.45
133(1)	56.05	1.802	1.60
120(2)	58.35	1.907	1.50
112(2)	68.6	2.756	1.94
115(1), 111(3)	81.5	6.29	3.9

origin as expression (40) would seem to require. This is considered to be due to the finite size of the diffracting sample. To correct for this increased size of the diffraction lines equation (40) is given the form

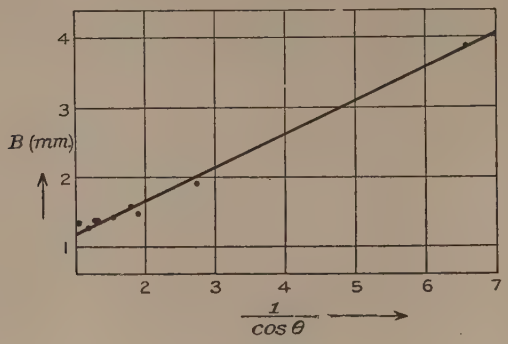


FIG. 199.

$$B = 2\sqrt{\frac{\log_e 2}{\pi}}\,\frac{\lambda}{D}\,\frac{1}{\cos\theta} + b \qquad \ldots\ (40a)$$

The angular (or absolute) value of B is such that 1 mm. upon the film is equal to $\frac{1}{28.5}$, consequently

$$B(\text{abs.}) = \frac{1}{28.5}\,B(\text{mm.}).$$

The application of the method of least squares to the data of Table I gives two constants [using B(abs.) in (40a)]

$$2\sqrt{\frac{\log_e 2}{\pi}}\,\frac{\lambda}{D} = \frac{1}{28.5}\cdot 0.478 \text{ and } b = \frac{1}{28.5}\cdot 0.727$$

Taking the wave length of the copper K-alpha line as 1.54A°, D then becomes

$$D = 2\sqrt{\frac{\log_e 2}{\pi}} \cdot \frac{1.54 \times 10^{-8}}{0.0168} = 8.62\mu\mu = 86.2\text{A}°.$$

This preparation was specified by the maker (Heyden) to have D = 10 $\mu\mu$. Since the unit cube of gold (containing four atoms in a face centered arrangement) is 4.07A° on a side, this particle size is equivalent to that of a cube containing 21.2 unit cells on a side:

$$D/a_0 = 86.2 \div 4.07 = 21.2.$$

Another gold preparation gave D = 18.6A°. A cube of gold having this length of edge would contain only 380 atoms. Gold crystals of this size, nevertheless, gave a diffraction pattern having lines identical in position with those of the macrocrystalline precipitate; but unless a wave length longer than the copper K-lines was used, the lines were too diffuse for accurate intensity measurements.

If a colloidal preparation is crystalline and has a uniform size of particles, then from the preceding example it is seen that its powder photograph offers a possible method for the determination of the crystal size. If the colloid is one containing particles of a variety of sizes the dimensions deduced by this procedure are averages. There are, however, certain difficulties in an accurate estimation of particle size in this way which the previous outline of method does not emphasize. The chief of these is the problem of accurately photometering for the half-intensity width of the diffraction lines; this is especially serious for all but the finest colloids because of the comparatively small distances to be measured. The method has thus far been applied only to the investigation of powders though probably very concentrated suspensions could also be used. The maximum size of particle which can be investigated with profit has not yet been ascertained; but it seems probable that this upper limit is set by a cube perhaps one to two hundred atoms on a side. This procedure, whatever its limitations may prove to be on more extended investigation, should furnish a fruitful source of information concerning not only the character of different colloidal substances but also the mechanism of crystal growth from solution and from material in the amorphous state.

A few observations bearing upon this latter question have already been made. It has been shown, for instance, that metallic sulfides when precipitated from aqueous solution give no diffraction pattern though the sols that can be produced from these sulfides are already crystalline (*1922*, 41). Aluminum hydroxide, when precipitated in the cold is not crystalline, but in an aged gel or in one which has come out of a hot solution the

formation of minute crystals has already taken place (*1922*, 41). The apparent discrepancies (*1917*, 11; *1920*, 52) in the behavior of aged silica gels probably have a similar explanation. Precipitates of the silver halides (*1922*, 41), on the other hand, have not been produced in an amorphous condition.

TABLE II. A CLASSIFICATION OF THE DIFFRACTION PHENOMENA OBSERVED FROM VARIOUS SAMPLES OF CARBON

1.	Graphite. Ceylon. Flaky. 0.1% ash.	IV
2.	" Sang Si, China.	
3.	" Huando, Korea.	
4.	" Crystalline mass of natural graphite (impure).	
5.	" Ceylon. Crystalline.	
6.	" Bohemia. Powder.	
7.	" Artificial. Powder, from Kahlbaum.	
8.	" Ceylon. Powder.	
9.	" Artificial. Powder, Acheson. 0.70% ash.	I
10.	" Korea. Crystalline mass.	
11.	" Takashimizu Etchyu, Japan. Crystalline.	
12.	Lime Nitrogen Carbon. Powder. 0.67% ash.	
13.	Graphite. Satsuma, Japan. Flaky powder. 0.14% ash.	
14.	" From Kahlbaum.	
15.	Carbon, catalytic decomposition of CO by Fe at 400–500°. Fine powder.	
16.	Graphite, from gray cast iron. Flaky powder.	II
17.	" from Japanese charcoal pig iron. Flaky powder. Ash less than 0.2%.	
18.	Temper carbon, from black hearted malleable castings. Powder.	
19.	Graphite, Artificial. Process of making unknown.	
20.	Retort gas-carbon. Amorphous mass. Ash 0.20%.	
21.	Coke. Gas oven. Amorphous mass. Ash 2.23%.	
22.	Carbon. By catalytic decomposition of C_2H_2 (by passing over treated Cu and purifying). Sooty powder.	III
23.	Carbon. By catalytic decomposition (see 22) of CS_2. Sooty powder.	
24.	Sugar carbon. From Kahlbaum. Powder.	
25.	" " By charring cane sugar and heating product in N_2 for four hours at 900°C	
26.	Charcoal. Magnolia.	
27.	Acetylene soot. By incomplete combustion.	
28.	Lamp black, commercial.	
29.	Sugar carbon. Made by dropping crystalline sugar into conc. H_2SO_4; chlorinated. Powder.	
30.	Sugar carbon. Made by adding conc. H_2SO_4 to solution of sugar; chlorinated. Powder.	
31.	Charcoal. Bamboo.	
32.	" Magnolia.	
33.	Animal charcoal. Amorphous mass.	
34.	Colloidal carbon. No. 5, suspended in 1% solution of tannic acid for 6 days. Allowed to stand 5 days and suspended C collected by centrifugal precipitation.	

A study (*1922*, 6) has been made of 34 samples of carbon from different sources to determine their crystallinity and the relative sizes of the crystalline particles composing them. All preparations showed one or more bands or lines coinciding with the positions of the lines of graphite. Thus not any of the carbons were amorphous though in some photographs the bands had breadths indicative of extreme minuteness of the crystals. Unfortunately the appearance of the "liquid pattern" is unknown under the experimental conditions of these observations (they were made with tungsten radiation) and it is consequently impossible to link up the very broad bands found from some carbons with this other sort of non-crystalline diffraction pattern. Four different types of photographs from these carbons are distinguished. To Type I belong those specimens giving the sharp powder lines characteristic of crystals very large compared with the wave length of the X-rays. The diffraction maxima in patterns of Type II are broadened but still plainly distinguishable. Where this widening has been carried to the point of yielding indistinct haloes, the pattern is grouped with Type III. In many graphites, presumably due to their platy nature, the crystals arrange themselves more or less completely under pressure and give rise not to a perfect powder photograph but to an approach to the "fibre pattern" (page 406); such materials belong to Type IV. From their nature it will be clear that Types I, II and III grade by degrees into one another. A sequence of these carbon samples in the order of decreasing sharpness of their diffraction effects is shown in Table II.

The Diffraction Effects from "Semi-crystals."—A crystal is built up by the parallel and indefinitely extended repetition of its unit cells. A solid in which the units have a perfectly haphazard arrangement with respect to one another is "amorphous." Various types of regularity between these extremes can be imagined. By "semi-crystals" are to be understood these hypothetical—or real—sorts of groupings. Preparations like the anisotropic silica and alumina obtained by the careful decomposition of various minerals seem to show the actual existence in nature of "semi-crystalline" substances. Possible types of this partial regularity are illustrated in Figure 200. For simplicity it is assumed that the construction unit, which in many cases can be taken as the chemical molecule, has the shape of an elongated rectangular prism (A of Figure 200). In a crystal these units would be arranged as in B; in an amorphous solid on the other hand they would be haphazardly grouped together. A simple sort of regularity would be achieved if they have only the long axis in common (C). Such a grouping might conceivably be formed, for example, by the haphazard sticking together of molecules of compounds composed of long paraffin chains. A more regular arrangement would be obtained

if the units are parallel to one another after the fashion of D. A still nearer approach to a crystal is shown in E and a somewhat different grouping for elongated units at F. Variations from these structures might have, for instance, a top aspect like D but a side view like that of the perfect

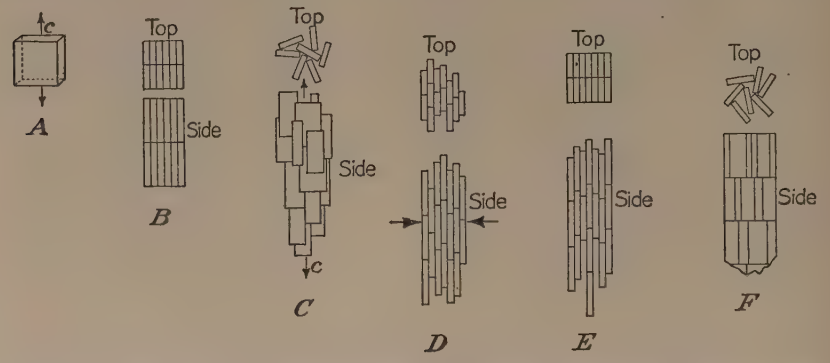


FIG. 200.—Possible types of arrangements of the units in imaginable "semi-crystals."

crystal B, or another might resemble D if all the units of the latter were turned haphazardly about the arrows as an axis.

The behaviors of these groupings towards X-rays would be very different. The action of the crystal B has been discussed in the preceding chapters. The arrangement of C, though the units have a direction in common, does not exhibit any constant interatomic distance; consequently no diffraction effects will arise from the interaction of rays scattered by the different units and it would be indistinguishable from an "amorphous" grouping. In D, and F, there is a constant distance between parallel planes and if there are enough planes it should be possible to obtain a single sharp reflection (and its higher orders) from them. Regularity exists in two directions at right angles in E so that a powder photograph from such a material would show additional reflections (and their higher orders).

The cells used in this discussion are highly artificial and undoubtedly would never even approximately accord with the physical realities in any "semi-crystals" which may exist. They serve, however, to illustrate types of regularity imaginable for less simple construction units and the nature of the diffractions produced by them.

Powder photographs of the oleates of potassium, sodium and ammonium are said (*1923*, 24) to show only three diffraction lines which are considered to be three orders of a single reflection. Recently more extensive studies (*1923*, 69, 69a, 81a) have been made of photographs from several of the higher fatty acids and other long chain carbon compounds.

These photographs were not powder photographs but were reflections from a sheet obtained by allowing the acid to solidify as a thin layer upon a glass plate. It is important to determine whether the single sharp reflection (and its higher orders) that is thus observed is due simply to the special orientation of the crystals with respect to the glass or whether as in the alkaline oleates it is also a characteristic of a true powder photograph of these compounds.[1] Besides the sharp lines two diffuse bands are found in practically the same positions for each substance. The bands appear to resemble the "liquid bands" produced by most liquids and glasses and the discovery of their origin will contribute largely towards a satisfactory knowledge of these compounds. For potassium oleate (*1923*, 24) the spacing corresponding to the sharp lines is 43.5A°. Since this value agrees closely with the determined thickness of the soap bubble films of this substance, the diffraction data have been thought (*1923*, 24) to show that the oleates have a structure resembling type F of Figure 200. This spacing and the ones measured for many of the other compounds are much greater than those which are calculated using the customary interatomic distances and making the assumption that all of the atoms are placed end to end in one long chain. If these substances are truly crystalline and if,

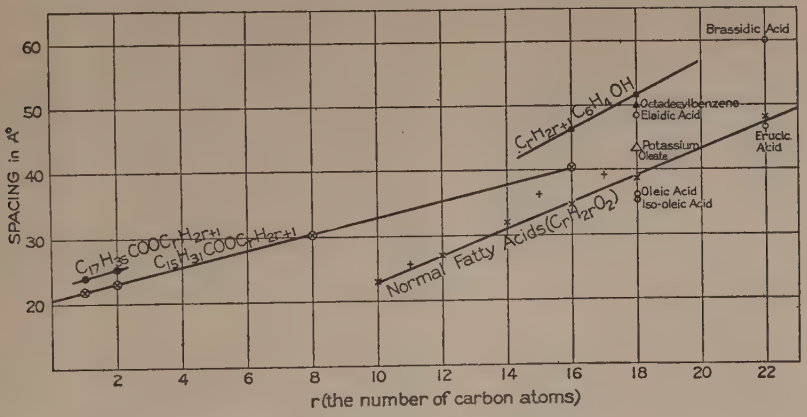


FIG. 201.—Spacing data upon fatty acids and other long carbon chain compounds.

as is probably the case, the chosen interatomic distances are approximately correct when applied to these substances, this observation seems to show that more than one molecule are contained within the unit cells (*1923*, 69). The spacing data upon the various long carbon chain compounds yet studied are collected in Figure 201. The straight line passing through

[1] Another study (*1921*, 11a) has been made of various fatty acids and their lithium salts; no data of any sort have, however, been published.

the points for the normal fatty acids containing even numbers of carbon atoms shows (*1923*, 69) that, at least approximately, their spacings increase by a constant amount with increase in the number of *pairs* of carbon atoms; this increase is seen to be very nearly 4A° per carbon pair. The data (*1923*, 69a) upon pentadecylic ($C_{15}H_{30}O_2$) and margaric ($C_{17}H_{34}O_2$) acids suggest that a different rule operates for the odd numbered than for the even numbered carbon acids; more results are, however, needed for the odd numbered acids. Similarly the spacings of the esters (*1923*, 81a) of palmitic ($C_{16}H_{32}O_2$) acid (and apparently also of stearic acid) increase by a constant amount, at least for the esters containing an even number of carbon atoms in their radicals. The increase in spacing per pair of ester carbon atoms is about 2.4A°, a value very different from that found for corresponding increases in the length of the carbon chain. These facts have been made the basis for speculations (*1923*, 69a) upon the shapes of carbon chains; data upon many more compounds, as well as a better idea of the nature of the solid acids, are necessary before these suggestions can be taken as probably correct.

When the mineral gillespite, which is a complex silicate of potassium and barium, is extracted with hydrochloric acid all of the metal atoms are removed and the water content is increased. The resulting insoluble portion is not optically isotropic, as might be expected, but shows like the original gillespite a uniaxial character. Only one diffraction line has been found in the powder photograph of this anisotropic insoluble residue.[1]

"Liquid crystals" are said to have no lines in their powder photographs (*1921*, 53); their Laue photographs also yield no evidence for a crystalline structure (*1921*, 68, 69). Whether this indicates the existence in these liquids of a regularity not greater than the sort portrayed in C of Figure 200 or whether the anisotropy of "liquid crystals" has a totally different explanation is not definitely answered by the experiments thus far carried out (see page 386).

The preceding experimental results suggest that powder patterns are sometimes obtained which contain only a single reflection. Even if the needed additional experiments confirm this fact extreme caution would be necessary in interpreting these data in terms of such "semi-crystals" as have been discussed. Whatever may prove to be the correct explanation of these patterns, the results already attained from the study of the fatty acids and esters show that the extension of these investigations will furnish data of great interest.

[1] From unpublished observations by W. T. Schaller, E. S. Larsen and the writer.

Diffraction Effects from Non-crystalline Materials

X-ray Diffraction Effects from Liquids and Glasses.—The powder photographs of most liquids and glassy solids consist not of an amorphous scattering but of a series of one or more broad but distinct diffraction *bands* (*1916*, 6). Several photographs of typical liquids and glasses are reproduced in Figure 202; as they show, there is no distinguishable difference between the patterns from materials in the two states of aggregation.

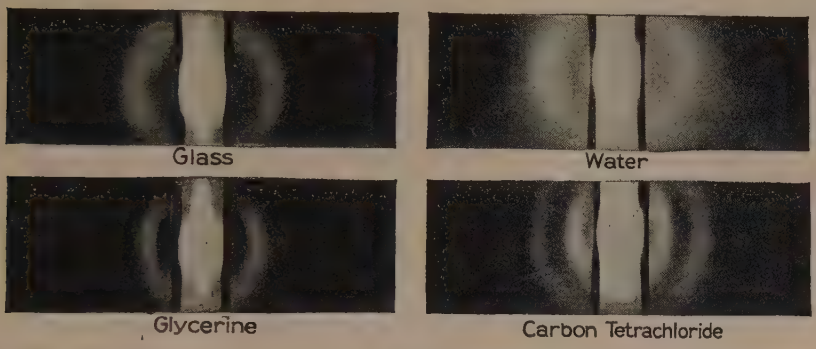


FIG. 202.—Typical X-ray diffraction patterns from liquid and glassy substances.

Not only their appearance but their possible sources suggest that the "liquid bands" have an origin very different from that of the diffraction lines produced by a crystalline solid. No experiments that have yet been made decide definitely what this source may be and at the present time there is no general agreement of opinion concerning it. Two types of explanation have been proposed. In the first place it has been imagined that these bands arise from the interference of rays scattered by the atoms within the chemical molecules of the liquid or glass (*1916*, 6). From this standpoint the bands do not arise from atoms regularly arranged with respect to one another in space but rather from constant distances between pairs of atoms. The proof that diffraction inside the molecules of a diatomic gas (*1915*, 7) would give rise to a series of broad bands shows that constant atomic separations may be sufficient to account for the observed haloes. On the other hand it has been urged that these diffraction effects are intermolecular in character. Two different explanations of this sort have been offered. It has been imagined that the bands arise from the rays scattered by the molecules which even in the liquid state are more or less regularly arranged with respect to one another (*1922*, 51). The other suggestion (*1923*, 75) sees these bands as the result of a scattering that is analogous to the scattering of light in a murky medium; the molecular

groupings responsible for these haloes thus may be similar to the arrangements postulated for the preceding (*1922*, 51) explanation but as chance associations of molecules, they would be only local in character and of the briefest duration.

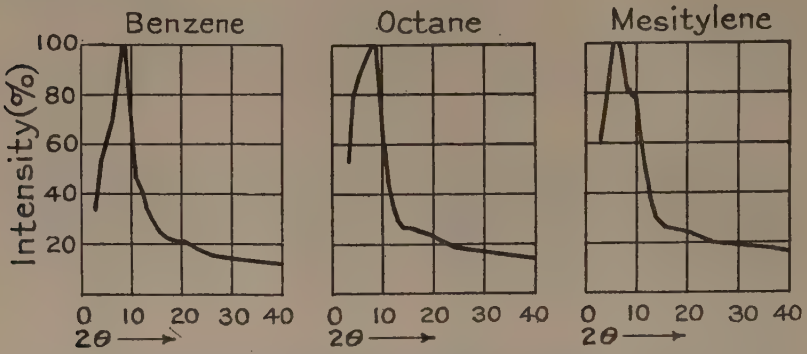


FIG. 203.—Plots showing the results of spectrometer measurements upon the three liquids benzene, octane and mesitylene (after Hewlett).

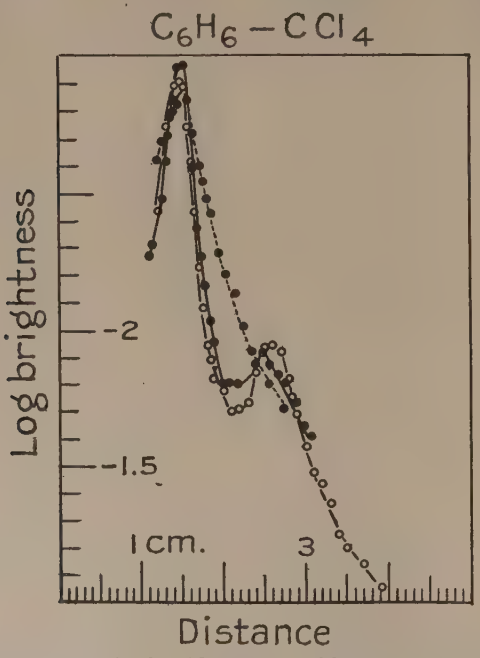


FIG. 204.—Photometer curves for liquid patterns of benzene, carbon tetrachloride and their 1 : 1 (by volume) mixture. The curve through the open circles is for carbon tetrachloride, the dotted curve is for benzene and the full line is the mixture curve. The abscissas are distances upon the film measured from the central undeviated image.

The "liquid patterns" have been obtained from several liquids, both inorganic and organic. Ordinary glasses, silica glass, amorphous silica, collodion and bakelite are amongst the solid materials that give these bands. Data for the liquids examined are reproduced in Table III and in (*1923*, 93) Figures 203 through 207.

TABLE III. THE POSITIONS OF LIQUID BANDS

SUBSTANCE	ANGLE OF DEVIATION	WAVE LENGTH	OBSERVER
Benzene	8.5°	0.712A°	(*1922*, 45)
Benzene	18	1.54	(*1916*, 6; *1922*, 51)
Octane	8.1	0.712	(*1922*, 45)
Mesitylene	4.1; 6.2	"	"
Ethyl alcohol	22	1.54	(*1922*, 51)
Ethyl ether	19	"	"
Formic acid	24	"	"
Carbon disulfide	13.23	0.712	(*1923*, 53)
Oxygen	12.5; 19.5	"	"
"	27	1.54	(*1922*, 51)
Argon	13.0; 18.9	0.712	(*1923*, 53)
"	27	1.54	(*1922*, 51)
Water	13.44	0.712	(*1923*, 53)
"	29	1.54	(*1922*, 51)
Nitrogen	11.34; 17.0	0.712	(*1923*, 53)

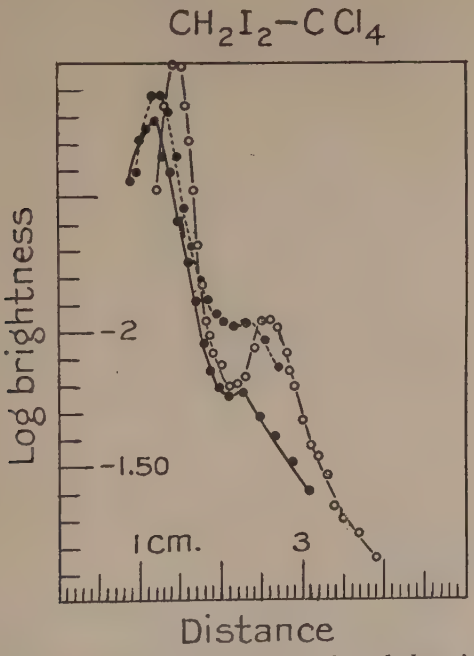


FIG. 205.—Photometer curves for liquid patterns of methylene iodide, carbon tetrachloride and their 1 : 1 (by volume) mixture. The curve for carbon tetrachloride passes through the open circles, the methylene iodide curve is dotted and the mixture curve is shown by the full line.

Unquestionably the most satisfactory procedure for photographing liquid diffractions would dispense with any container and employ directly a thin stream of the liquid. A photograph of liquid benzene (*1916*, 6) has been prepared in this manner. In all other measurements use has been made of cells or tubes of glass, collodion or other material equally capable of giving a liquid pattern. For this reason it is necessary to scrutinize with care the existing data. Some spectrometric observations have been published upon liquids contained within thin-walled celluloid

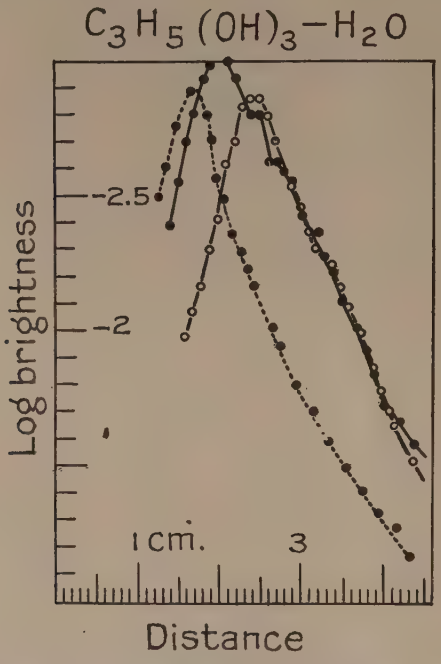


FIG. 206.—Photometer curves for liquid patterns of glycerine, water and their 1 : 1 (by volume) mixture. The dotted curve is for glycerine, the open circles are observation points for water and the full curve is that of the mixture.

tubes (*1922*, 45); it has also been found that cells with sides made of the thinnest sheet celluloid (*1923*, 93) do not give observable diffractions within the time required to register the diffraction pattern of a liquid they may contain. Especially in dealing with organic liquids, however, these cells have a very limited usefulness on account of the rapidity with which they are destroyed.

Powder photographs have been prepared from several compounds which form "liquid crystals" (*1921*, 53). At a sufficiently high temperature these substances are clear liquids but as they are cooled they reach points (the "clarification" temperatures) at which they become murky

and optically anisotropic. On further cooling through this turbid region the melting points are reached and crystalline solids are formed. The

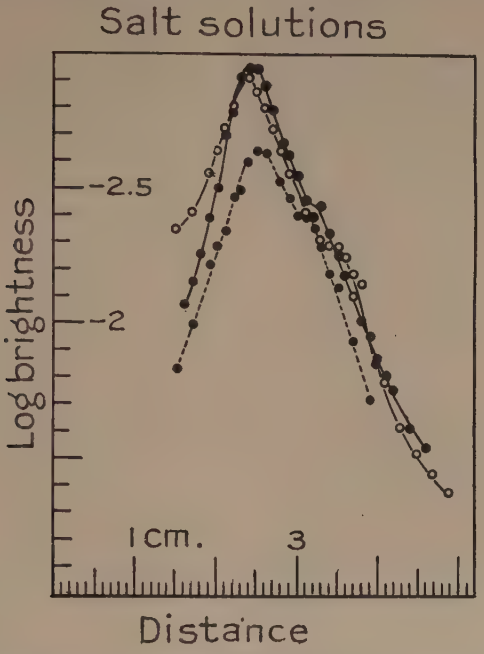


FIG. 207.—Photometer curves for water (full line) and for concentrated aqueous solutions of potassium chloride (dotted line) and iron ammonium alum (open circle curve).

results of photographs of compounds in these three conditions are summarized in Table IV. In all cases the turbid as well as the clear liquids yield only liquid patterns. Under the microscope the esters of cholesterol show the presence of what appear to be minute crystals; their failure to contribute a crystalline diffraction to the pattern of the murky stage is probably to be attributed to the predominance of the liquid phase. These

TABLE IV. DATA UPON "LIQUID CRYSTALS" (*1921*, 53)

SUBSTANCE	PHYSICAL STATE	DIFFRACTION PATTERN
p-azoxyanisol	solid	crystalline
"	turbid-liquid	liquid
"	clear-liquid	"
p-azoxyphenetol	solid	crystalline
"	turbid-liquid	liquid
Dianisalazin	"	"
Cholesterol proprianate	solid	crystalline
"	turbid-liquid	liquid
"	clear-liquid	"
Cholesterol benzoate	turbid-liquid	"

experiments prove that most of the liquid of a "liquid crystal" not only does not possess a crystalline arrangement but is devoid of any form of regularity which might give "semi-crystalline" diffractions. Beyond that they do not go.

Some of the observations upon liquid patterns have a distinct, if as yet not entirely conclusive, bearing upon their origin. The assurance that the phenomena are really ones of diffraction is given by the fact that the positions of the bands change with the wave length of the X-rays that are employed (see Table III). Proceeding upon the assumption that they are produced within the molecules, calculations (*1916*, 6) have been offered to show that the bands of benzene are compatible with a molecule of reasonable size and shape. Liquid argon, which is undoubtedly composed of monatomic molecules, has been found to give (*1922*, 51; *1923*, 53) a clearly defined pattern. It has also been reported that mercury yields a liquid pattern (*1921*, 33); but an attempt to reproduce these effects by photographing (*1923*, 93) a suspension of mercury droplets in collodion showed only the bands of the collodion superimposed upon a much blackened field.[1] If the observed bands of argon actually arise from the liquid and not from its glass container, it seems necessary to look to intermolecular associations for at least their principal origins. Calculations have been made (*1922*, 51; *1923*, 53) which are supposed to show the existence of a definite close packing of the molecules in liquids. For these calculations it is imagined (1) that the molecules of a liquid are in the hexagonal closest packed arrangement of spheres [d], (2) that nevertheless they do not give rise to a crystalline diffraction but the positions of the bands they produce can be obtained by considering the interferences from a pair of molecules and (3) that in so doing use can be made of the expression describing the diffraction effects to be expected from the two atoms in the molecule of a diatomic gas. Proceeding from these assumptions an approximate agreement is found with the observed positions of the bands of some liquids (Table V). From certain aspects some of these assumptions are so unexpected that it is difficult to place a satisfactory evaluation upon such numerical coincidences as the data show.

Patterns have been investigated from a few pure liquids and their mixtures (*1923*, 93). If the liquid bands were of a purely intramolecular nature the diffraction of a mixture of two liquids ought to be essentially the sum of those of the pure liquids themselves. This will not be true if the diffraction arises from pairs of molecules (*1922*, 51; *1923*, 53) but it may not be incompatible with the idea of temporary regular associations of molecules (*1923*, 75) if these regularities extend over several molecules.

[1] An amorphous scattering from mercury may, like the scattering from solid potassium, result from large amplitudes of the thermal vibrations of its atoms.

TABLE V

A. Using Molybdenum K-radiation ($\lambda = 0.712$A°) (*1923*, 53)

SUBSTANCE	ANGLE OF DEVIATION	OBSERVED "SPACING"	$1.33\sqrt[3]{\frac{M}{F}}$
Oxygen	12.50°	4.0A°	4.0A°
Argon	13.0	3.85	4.1
Water	13.44	3.73	3.6
Nitrogen	11.34	4.42	4.4
Carbon disulfide	13.23	3.8	5.2
B. Using Copper K-radiation ($\lambda = 1.54$A°) (*1922*, 51)			
Oxygen	27°	4.0	4.0
Argon	27	4.0	4.1
Benzene	18	6.0	5.9
Water	29	3.75	3.6
Ethyl alcohol	22	4.9	5.2
Ethyl ether	19	5.7	6.2
Formic acid	24	4.5	4.5

The data thus far accumulated (*1923*, 93) for liquid mixtures are shown in Figures 204, 205 and 206. Within the limit of error of the observations (Figure 207) the patterns (*1923*, 93) of water are identical with those of concentrated aqueous solutions of potassium chloride and iron ammonium alum. These data agree with the statement that the diffraction pattern of a liquid mixture is the sum of the diffractions of its pure components. The bands of these pure liquids have, however, positions so close together that the available experiments do not prove that new mixture bands cannot lie between them. The possible existence of such new bands could probably be determined by increasing the resolution through a decrease in the thickness of the sample and the width of the spectrograph slits.

The alkaline oleates (*1923*, 24) are said to yield liquid bands as well as the lines of a "semi-crystal." If both patterns are due to the oleates, a study of "semi-crystals" will also throw light upon the nature of the liquid diffractions. Similar diffuse lines occur in the patterns of fatty acids and esters (*1923*, 69, 69a, 81a).

It is evident from the preceding discussion that the available experiments do not permit of a final decision concerning the origin of liquid bands. If argon actually gives rise to liquid bands, interference between the rays scattered by the atoms of a single molecule must be a minor factor. Additional experiments are needed, however, to establish the nature of the order in molecular arrangement which is then responsible for the observed effects.

Amorphous Scattering from Non-crystalline Materials.—The fact that liquids and glasses, as well as crystals, produce definite diffraction effects leaves only a very small class of substances among which to seek materials devoid of any regularity. The possibility of amorphous metal as the source

of the general scattering observed from polished surfaces has been mentioned. It has been said (*1923*, 22) that porcelain gives besides the lines of sillimanite a general blackening which may be due to a large admixture of amorphous material. Precipitates of metallic sulfides and hydroxides from cold aqueous solutions also are considered to show only an amorphous character (*1922*, 41). The mineral gadolinite, when it is optically isotropic, appears to be completely amorphous (*1922*, 55). In these last cases, however, the data do not give assurance of the non-existence of liquid patterns.

It is not known whether diffraction phenomena can be produced by the electrons within a single atom. If they are possible, none would be expected except with short wave lengths. They would then be most naturally sought amongst the few materials which give an amorphous scattering of X-rays of the usual length.

Summary of Types of X-ray Diffraction Effects

Three distinct types of X-ray diffraction effects have been encountered —crystalline, liquid and "amorphous." Their interrelations and sources are incompletely known as yet but the available knowledge can be expressed as follows:

I. Crystalline Diffraction Patterns.
   - A. Perfect crystalline diffraction (a series of sharp lines in a powder photograph). From crystals having a size very great compared with the wave lengths of X-rays.
   - B. Imperfect crystalline diffraction.
     1. Effects (usually more or less hazy) arising from strained and distorted crystals and crystalline aggregates.
     2. Broad crystalline diffraction (broadened lines in the positions occupied by the lines in the pattern of a perfect crystal). From crystals the size of which approaches that of the wave length of X-rays.
     3. "Semi-crystalline" diffraction (one or two sharp lines, and their higher orders, in the powder photograph). To be expected from materials that possess atomic regularity in less than three directions.

II. Liquid (or Glassy) Diffraction Patterns (a series of one or more broad diffraction bands).
   - A. Probably from all liquids.
   - B. From glasses.
   - C. From some "amorphous" solids (such as amorphous silica).

III. General or "Amorphous" Scattering (a generally distributed blackening of the photographic plate).

A. From some crystalline solids and perhaps from some liquids (presumably those with large amplitudes of thermal vibration).

B. Probably from purely amorphous solids (if they exist).

Chapter XV. Some Applications of Diffraction Information

The results of crystal analysis have already been of influence in many branches of science. This range of usefulness is so great that its adequate discussion would require the space of a separate monograph. For this reason alone the present chapter will be limited to a very qualitative consideration of a few topics of timely or especial interest.

The Bearing of Crystal Structure Data upon the Existence of Molecules and the Nature of Valence.—One of the most interesting contributions of crystal structure knowledge arises from its bearing upon the nature of valence relations in the solid state. From such sources as the Gay-Lussac Law of volumes and the kinetic theory of gases, as well as numerous results of recent physical research, there is unmistakable evidence for the existence of chemical molecules in gases. The extension of the gas laws to dilute solutions also has indicated that the solute is distributed in some cases throughout the solvent as small and constant associations of atoms. Furthermore it seems impossible to imagine other than a molecular constitution for typical organic compounds whether they are in the physical state of gas, liquid or solid. There has, however, been no authentic information to show that such constant associations of atoms as are commonly understood by the term chemical molecule exist in other liquids and solids. The practically universal assumption by chemists that under all physical circumstances the normal condition is one in which a few atoms are associated together as molecules has thus been an experimentally unwarranted extrapolation from the existing knowledge. For this reason evidence for the non-existence of chemical molecules in most inorganic solids need not be in contradiction of previous experiments.

From crystal structure data it seems quite certain that no molecules are to be distinguished in such crystals as sodium chloride. If a sodium and a chlorine atom were bound together as a molecule in rock salt, then since the forces holding them together would be greater than those acting between either atom and any other within the solid mass, their distance apart would be different from other interatomic distances within the crystal. A study of the structure of sodium chloride crystals, however, shows that each chlorine atom is surrounded by six equally distant sodium

atoms and each sodium atom by six equally distant chlorine atoms (Figure 167). The repetition of this equality in atomic separations makes the entire crystal the next physical entity larger than the atoms of which it is composed. A reference to the structures of the other inorganic crystals which have been investigated shows that in most of them the usually assumed chemical molecules can not be distinguished. Nevertheless wherever such atomic associations as the sulfate, carbonate, or nitrate groups are present they can be identified within the crystal structure. A few inorganic compounds have non-polar and other physical properties which suggest that definite molecules are present in their crystals. Tin tetraiodide is such a substance and molecules of SnI_4 can be distinguished in its crystal structure. Likewise the molecule can be found within crystals of hexamethylene tetramine ($C_6H_{12}N_4$), the only truly organic compound the structure of which has yet been adequately and completely elucidated.

Crystal structure information thus distinguishes between three types of crystals. In the first group, of which sodium chloride is typical, no distinctive association of atoms short of the entire crystal can be observed. All of the known examples of this class are inorganic salts (including oxides, sulfides, etc.). Of a second sort are crystals within which may be detected what might be termed "submolecular" associations of atoms. The sulphate, nitrate or chloroplatinate ions are amongst these sub-molecular groups; others are water or ammonia molecules, and such larger association of these molecules with the metal atoms in hydrates and ammoniates as $[NiCl_2 \cdot 6NH_3]$. In the third category are to be found those inorganic and organic crystals which can be considered to be made up of molecules. Tin tetraiodide, hexamethylene tetramine and the cubic trioxides of arsenic and antimony are examples of these molecular crystals.

A reference to the structures of certain crystals shows, however, that in many cases these groupings are not conspicuous: Their identification is rather in the nature of an observation which is not incompatible with the results. In other words, if nothing were known of the chemical properties of such a crystal in advance of its structure determination it would not be safe to say from its atomic arrangement that certain atoms formed distinct groupings. The impossibility of working back in this manner from the crystal structure data to conclusions concerning the substance itself is strikingly illustrated by a comparison of silver molybdate (Ag_2MoO_4) with the magnesium aluminum spinel ($MgAl_2O_4$). These two crystals have identically the same atomic arrangement, with magnesium and molybdenum atoms, and silver and aluminum atoms occupying the corresponding positions within the unit cubes. All chemists would probably agree that the former compound is built up of silver atoms, or

ions, and molybdate (MoO_4) groups, or ions; and they would see the clustering of four oxygen atoms about each molybdenum atom as evidence for the continued existence of molybdate groups in the solid state. Yet this same reasoning would find an indication of the presence of a chemically unthinkable MgO_4 group in the corresponding association of four oxygen atoms about the magnesium atom of the spinel. From such an example as this it is evident that conclusions cannot be drawn from crystal structure results concerning the existence of sub-molecular groupings of atoms. It appears perfectly legitimate, however, to require that atomic groups which are stable in solution and other states of aggregation shall be continued in the crystal. For instance in a crystal containing the sulfate group, it appears justifiable to require that four oxygen atoms shall be intimately associated with each sulfur atom. Too few examples of molecular crystals have been examined to show how readily distinguishable will be their molecules.

In view of the preëminent place which the idea of valence has played in the development of chemical theory, it is natural to inquire whether a connection can be observed between the commonly accepted valence of atoms and the structures of the crystals containing them. For non-molecular crystals the existing data are sufficient to answer this question emphatically in the negative. The following examples will make this entirely clear. Sodium chloride and magnesium oxide, as typical of compounds composed of two univalent and two divalent atoms respectively, have identically the same atomic arrangements. In cesium fluoride, with the sodium chloride arrangement, each univalent atom is surrounded by six equally distant univalent atoms of the opposite kind but in the chemically related cesium chloride, each atom has eight of the other sort equally distant from it. Each copper atom in cuprous chloride, also a compound of two univalent atoms, is surrounded by four chlorine atoms and each chlorine atom by four copper atoms. Such examples as these are almost as numerous as are the available data for simple crystals. The absence of an obvious connection between valence and atomic arrangement is also to be seen amongst the more complicated groupings. Thus in the structurally isomorphous crystals of magnesium aluminum spinel ($MgAl_2O_4$), potassium zinc cyanide ($K_2Zn(CN)_4$) and silver molybdate (Ag_2MoO_4), trivalent aluminum and the univalent potassium and silver atoms occupy analogous positions in the crystal, as do likewise both the divalent magnesium and zinc and the hexavalent molybdenum on the one hand and the divalent oxygen atoms and the univalent cyanide radicals on the other. From such observations it would have been necessary to conclude that the picture of valence bonds as definite individual links between atoms does not apply in these solids if the recognition of the

electron as the probable bonding agent in atomic combinations had not already indicated it.

Crystal structure results are capable of supplying information concerning the equivalence of the bonds joining an atom to those about it. A consideration of the atomic arrangement in tin tetraiodide (SnI_4), for instance, shows that three of the iodine atoms are equivalent (i.e., are identically related to their surrounding atoms) but different from the fourth. Similarly it is clear from the structure of calcite ($CaCO_3$) that the three oxygen atoms must be alike and consequently that such a formula as $CaO \cdot CO_2$ is without justification. Many conclusions of this sort can be drawn from a knowledge of the symmetry of a crystal even before its atomic arrangement has been studied. Thus the five oxygen atoms of crystalline phosphorus pentoxide cannot be equivalent because no group of five, or an integral multiple of five, equivalent positions is permitted by any kind of crystalline symmetry. The numbers of equivalent points in any arrangement having orthorhombic symmetry are limited to 1, 2, 4, 8, 16 and 32. Since KNO_3 and $CaCO_3$, as aragonite, have this symmetry and since none of these numbers are multiples of three, it must immediately be concluded that in neither of these crystals are the three oxygen atoms alike in their relations to the other atoms of the crystal. For the same reason it can be concluded that since benzene forms orthorhombic crystals it is impossible for all six of the carbon atoms of its molecule to be equivalent in the solid state. Applications of this principle can be multiplied almost without limit. It is to be noted that the only assumption made is the one which underlies all use of mathematical in physical crystallography—that the atoms of a crystal occupy positions in space which conform to its symmetry. At the same time, however, it is necessary to bear in mind the fact that it is not now possible to state precisely how much chemical significance attaches to these non-equivalences.

Crystal structure studies have thrown some light upon the distribution of atoms associated together through the operation of "secondary valence." For many years the compound cesium dichloroiodide ($CsCl_2I$), as typical of the alkali polyhalides, was considered to be a "double-salt" of cesium chloride and iodine monochloride (ICl); more recently, however, and on the basis of studies of its behavior in solutions it has been treated as the cesium salt of the hypothetical acid $HICl_2$. An investigation of its crystal structure shows that the two chlorine atoms must be identically related to an iodine atom (if as is probable the determined structure is correct). This arrangement is in direct contradiction with the "double-salt" interpretation and favors the existence of ICl_2 groups within the crystal. It is likely that two fluorine atoms are equally associated with each hydrogen

atom in potassium hydrogen fluoride (KHF_2), and perhaps also in the sodium hydrogen fluoride ($NaHF_2$). In the hexammoniate of nickel chloride [$NiCl_2 \cdot 6NH_3$] the six ammonia groups, which are assumed to be held within the crystal by the operation of secondary valency forces, have geometrically identical relations to a central nickel atom; these relations are the same as those maintained towards a platinum atom by the six chlorine atoms in the isomorphous ammonium chloroplatinate [$(NH_4)_2PtCl_6$]. In the hexahydrate of zinc bromate the six water groups are all equivalent and have a similar arrangement, probably about the zinc atom. There has been discussion in the past as to which atoms in a hydrate or ammoniate are most intimately associated with the water or ammonia groups. The structure of the hexammoniate nickel halides requires that all six ammonia groups be equivalent to one another and favors the assumption that these molecular groups are most closely associated with the metal atoms. In the alums likewise the twelve water molecules fall into two groups of six equivalent molecules; and it is compatible with the atomic arrangement, though geometrically not a requirement of this structure, to imagine one group to be arranged about the alkali metal atom and the other to belong to the trivalent atom.

From numerous sources it has become apparent that the valence relationships of atoms can be accounted for in terms of the number and behavior of the least tightly bound ("outermost") electrons in atoms. Two ways suggest themselves by which electron interaction can endow atoms with definite units of combining power for other atoms: (1) one or more electrons may be held in common, or shared, by two atoms, or (2) electrons may be transferred completely from one atom to another. In the latter case the atom which loses electrons becomes positively charged (electrically) and the atom acquiring electrons assumes a negative charge. The sharing of electrons, on the other hand, does not involve the development of charged atoms. The presence of negatively charged atoms in solutions and melts shows clearly that a strong tendency exists for atoms to attach electrons beyond the number required to neutralize the positive charges of their nuclei. These charged atoms (ions) are obtained in solution by dissolving compounds built up of strongly electronegative (electron-acquiring) and strongly electro-positive (electron-losing) atoms. Most of the crystals with non-molecular structures are of this sort and it is in accord with their other properties to suppose that their atoms are electrically charged in the solid state as well as in solution. If this hypothesis is adopted no contradiction exists between the present-day information concerning the nature of valence and the results of the crystal analysis of salts of strongly electropositive and electronegative atoms. An attempt has been made to prove the existence of charged atoms

in crystals of lithium fluoride from measurements of the relative intensities of X-ray reflections from various planes (*1918*, 11). Such a proof involves the assumption of a knowledge of the laws of scattering for this crystal. Inasmuch as these laws are not accurately known at present, the possibly better agreement between observed intensities of reflection and those calculated from "laws" assuming the existence of lithium and fluorine ions (instead of neutral atoms) cannot be more than an indication of the probable presence of charged atoms within the crystal. The same lack of validity attaches to similar proofs of the non-existence of shared-electron bonds in the diamond and other crystals (*1918*, 11; *1920*, 37). Only atoms which hold their electrons with a considerable tenacity and tend to acquire more beyond the number necessary for electrical neutrality may be expected to share electrons with one another. Thus electron-sharing bonds are to be sought only in compounds which involve the close association of amphoteric or electronegative atoms. If all of the atoms in a crystal are held together by electron-sharing bonds, then it may or may not contain molecules. For instance, if the atoms in the diamond are united by such bonds, every atom will share electrons with each of the four carbon atoms around it, and this continued indefinitely will make the entire piece of crystal a single molecule; a sharing of electrons between neighboring atoms, on the other hand, can take place entirely within a molecule of composition $C_6H_{12}N_4$ in crystals of hexamethylene tetramine. It must be emphasized that no available crystal structure evidence either proves or disproves the existence of electron-sharing bonds between atoms.

Various attempts have been made to link up particular atom models involving amplifications of these ideas of valence with determined crystal structures and even to predict structures in advance of their X-ray analysis. Not enough is known, however, about the structures of either atoms or crystals to make these attempts of value to crystal analysis itself.

More important are the efforts[1] to calculate the physical and chemical properties of crystalline compounds. Thus far a large part of these attempts have been directed towards a study of the alkali halides. So little is yet known about the interior of atoms, and especially about their loosely-bound electrons, that a lengthy consideration is required to show how much of the calculated agreement with experiment is due to the correctness of the particular assumptions used and how much is due simply to the additivity of properties in this series of crystals. Whatever may be the permanent worth of these efforts

[1] See the numerous papers by Born, Landé, Fajans, Herzfeld, and others beginning with (*1918*, 4).

in their present form, they are of the greatest importance as forerunners in opening up one of the ways through which chemistry and physics ultimately will be merged.

Crystal Structure and the Shapes of Atoms.—The question of how far the symmetry in the arrangement of its constituent parts extends into the intimate structure of a crystal continues to be a puzzling one. It has already been emphasized that the fundamental assumption underlying all present-day applications of mathematical crystallography is that the spacial arrangement of the atoms in a crystal must conform to its symmetry. The hydrogen atoms of ammonium groups in the alums and other salts probably do not occupy positions demanded by the observed crystal symmetry; otherwise there is no reason from the existing data to doubt the correctness of this basic postulate. From the available information it is not clear whether these hydrogen atoms occupy fixed equilibrium positions and thus introduce merely a formal contradiction of this assumption (owing to the ineffectiveness of hydrogen) or whether ammonium (and perhaps other) groups behave in their symmetry effects as if they were single entities. From many standpoints the latter possibility is the more probable one.

On various occasions it has been proposed [see for instance (*1915*, 15)] that not only the symmetry of their positions but the symmetries of the atoms themselves must agree with the observed crystal symmetry. No information exists which will prove whether or not this is correct, though observations like the ones just recorded for the ammonium group suggest that order in arrangement proceeds less rather than more deeply into the crystal structure than the atomic positions. Attempts have been made to ascribe some of the apparent disagreements between X-ray data and crystallographic symmetry, especially those from etch-figure observations, to low atomic symmetry; but detailed explanations on these grounds have not been offered and no simple ones seem forthcoming. The requirements of strict symmetry agreement between a crystal and its atoms calls for almost as many different forms of an atom as there are kinds of symmetry. For example it would necessitate a cubic calcium atom (or ion) in calcium oxide, a trigonal one in calcite ($CaCO_3$), an orthorhombic one in aragonite ($CaCO_3$) and a monoclinic or triclinic one in certain natural silicates and organic crystals. There is, however, no way of disproving this assumption from crystal structure data, especially if it is considered that the symmetry of an atom is at least as high as that of the most symmetrical crystal in which it occurs. Such a supposition of oriented atoms carries with it the consequence that atoms must have different symmetries in different crystals; for unless an atom which is sometimes in cubic and sometimes in hexagonal crystals is essentially

spherical and thereby devoid of distinctive shape, there is no way in which it can have within itself both of these sets of axes at the same time.

It has sometimes been urged [1] that the electrons of an atom have fixed positions of equilibrium about the central positive nucleus. Thus in deference to the tendency to complete groups of eight electrons in chemical combinations either by the loss or addition of electrons beyond the number required for neutrality, atom models have been proposed with electrons arranged about the nucleus at the corners of cubes or in pairs at the corners of tetrahedrons. Crystal structure data are capable of furnishing some information upon the question of the reality of such fixed electron positions for the chemically active electrons in atoms. For example (*1920*, 63), since the three oxygen atoms of the carbonate group in calcite are all alike, each must be bound in the same manner to the central carbon atom. If it is assumed that these atoms are united by sharing electrons, then six of the chemically active electrons of a carbon atom will lie in one plane and more or less in pairs which make 120° with one another; there is thus no reasonable approach to either a cubic or a tetrahedral arrangement. Consequently it is necessary to face the alternative that either the outside bonding electrons need not have a cubic (or tetrahedral) arrangement or else that such electron bonds do not exist between the carbon and oxygen atoms in calcite. Crystal structure determinations do not now offer a way of deciding definitely between these possibilities—though there is little physical and no real chemical evidence pointing to the existence of atoms of a fixed cubical, or any other, shape. Furthermore the many consequences of a choice seem to show that, at least for the present, it is wiser to retain the idea of electron-sharing.

The Hypothesis of Constant Atomic Radii.—Since the beginnings of crystallographic thought the sizes, shapes, and spacial distributions of the atoms in crystals have been subjects for speculation. A favorite hypothesis has been one which considers crystals to be composed of atoms of constant volume packed closely together. Sometimes the close-packing has been stressed, at other times the constancy of atomic volume has been emphasized as the principal determining factor. The wide divergence of the molecular volumes of dimorphous modifications of various substances shows immediately the impossibility of atoms of constant volume being closely packed together. The distances apart of atoms are given by crystal structure data and it has recently been suggested (*1920*, 12) that they are in accord with the assumption that crystals are built of closely packed atoms of "constant radii." The essence of this idea is contained in the statement that the distance between two atoms is always

[1] G. N. Lewis, J. Am. Chem. Soc. *38*, 762 (1916); I. Langmuir, ibid. *41*, 868 (1919) etc.

the same for the same mode of chemical combination and consequently "radii" from which the interatomic distances can be calculated can be assigned to each kind of atom. A test of this hypothesis is of importance because it or any other similar relation, if correct, would largely extend the range of crystals capable of being analyzed by existing methods. Numerous starting-points are possible for the calculation of these radii. The "radius" of a metal atom can be obtained immediately by halving the distance of closest approach of two atoms in a metal crystal; or the "radius" of the sulfur atom can be found in the same manner from the distance apart of two sulfur atoms in pyrite (FeS_2). If series of dimensions for various atoms in a number of crystals are calculated using these different starting-points, it is found that the results are not in agreement with one another. This in itself shows a variability in the radii. An idea of the extent to which such a constancy is approached for the available crystal structures can be had by reference to Tables I and II; these

TABLE I

DATA THAT ACCORD WITH AN HYPOTHESIS OF CONSTANT ATOMIC RADII

		Interatomic Distances	
Crystal	Between Atoms	Calculated	Observed
Li	Li–Li	3.00A°.	3.03A°.
LiH	Li–H	(2.05)	2.05
LiF	Li–F	2.12	2.07; 2.01
LiCl	Li–Cl	2.581	2.585
LiBr	Li–Br	2.746	2.74
LiI	Li–I	3.00	3.03
NaF	Na–F	2.35	2.34; 2.305
NaCl	Na–Cl	(2.814)	2.814
NaBr	Na–Br	2.976	2.975; 3.01
NaI	Na–I	3.23	3.235; 3.25
$NaNO_3$	Na–O	2.37 (if $u = \frac{1}{4}$)	2.388
KF	K–F	2.676	2.68; 2.69
KCl	K–Cl	3.136	3.13
KBr	K–Br	3.301	3.30
KI	K–I	3.556	3.55
KCN	K–(CN)	(3.27)	3.27
RbCl	Rb–Cl	3.30	3.30
RbBr	Rb–Br	3.466	3.465
RbI	Rb–I	3.72	3.68; 3.654
CsF	Cs–F	3.06	3.015
CsCl	Cs–Cl	3.52	3.568
CsBr	Cs–Br	3.686	3.724; 3.713
CsI	Cs–I	(3.94)	3.94; 3.966
MgO	Mg–O	(2.10)	2.10
$Mg(OH)_2$	Mg–O	2.10	2.09 (probably)
CaF_2	Ca–F	(2.368)	2.368

TABLE I—*Continued*

CaO	Ca–O	2.387	2.384
$CaCO_3$	Ca–O	2.387 (if u = $\frac{1}{4}$)	2.372
BaO	Ba–O	(2.74)	2.74
BaF_2	Ba–F	2.72	2.684
ZnS	Zn–S	(2.337)	2.337
ZnO	Zn–O	1.934	1.942
Cu_2O	Cu–O	(1.845)	1.845
CuCl	Cu–Cl	2.286	2.377; 2.32
CuBr	Cu–Br	2.451	2.52; 2.49
CuI	Cu–I	2.706	2.64; 2.63
AgCl	Ag–Cl	2.725	2.78; 2.76
AgBr	Ag–Br	(2.89)	2.89
Ag_2MoO_4	Ag–O	2.284	2.315
$CaCO_3$	C–O	(1.245)	1.245 (if u = $\frac{1}{4}$)
$MnCO_3$	C–O	1.245	1.275 (if u = 0.27)
Sn (gray)	Sn–Sn	2.734	2.798
K_2SnCl_6	Sn–Cl	(2.448)	2.448
$(NH_4)_2SnCl_6$	Sn–Cl	2.448	2.462
Ag_2MoO_4	Mo–O	(2.00)	2.00
Mo	Mo–Mo	2.72	2.72; 2.668
FeS_2	Fe–S	(2.254)	2.254
Fe	Fe–Fe	2.422	2.476
Fe_3O_4	Fe^{II}–O	1.851	1.797
MnS	Mn–S	(2.607)	2.607
$MnCO_3$	Mn–O	2.204	2.17 (if u = 0.27)
$Mn(OH)_2$	Mn–O	2.204	2.08–2.26 (2.19 is best)
K_2PtCl_4	Pt–Cl	(2.27)	2.27
$(NH_4)_2PtCl_6$	Pt–Cl	2.27	2.16–2.36
K_2PdCl_4	Pd–Cl	(2.29)	2.29
$(NH_4)_2PdCl_4$	Pd–Cl	2.29	2.34 (approximately)

TABLE II

DATA DISAGREEING WITH AN HYPOTHESIS OF CONSTANT ATOMIC RADII

		Interatomic Distances	
CRYSTAL	Between Atoms	Calculated	Observed
Na	Na–Na	3.46 A°	3.724A°
K	K–K	4.11	4.504
$K_2Zn(CN)_4$	K–(CN)	3.27	3.14
K_2PtCl_4	K–Cl	3.136	3.227
K_2PdCl_4	K–Cl	3.136	3.23
K_2SnCl_6	K–Cl	3.136	3.48
$CsCl_2I$	Cs–Cl	3.52	3.65
$CsCl_2I$	Cs–I	3.94	4.18
Be	Be–Be	(2.234)	2.234
BeO	Be–O	1.757	1.648 and 1.65 (if u = $\frac{5}{8}$)
Mg	Mg–Mg	2.92	3.22
Ca	Ca–Ca	3.494	3.926

TABLE II—*Continued*

DATA DISAGREEING WITH AN HYPOTHESIS OF CONSTANT ATOMIC RADII

CRYSTAL	Between Atoms	INTERATOMIC DISTANCES Calculated	Observed
Zn	Zn–Zn	2.588	2.93
$K_2Zn(CN)_4$	Zn–(CN)	2.514	2.715
Cd	Cd–Cd	3.44	3.30
CdO	Cd–O	(2.36)	2.36
$K_2Cd(CN)_4$	Cd–(CN)	2.94	2.80
CdI_2	Cd–I	3.22	2.98
Cu	Cu–Cu	2.41	2.542
Ag	Ag–Ag	3.288	2.866
Ag_2O	Ag–O	2.284	2.06; 2.04; 2.03
AgI	Ag–I	3.145	2.81 and 2.825
Diamond	C–C	1.21	1.542
Si	Si–Si	2.194	2.352
$(NH_4)_2SiF_6$	Si–F	(1.718)	1.718
$NaNO_3$	N–O	(1.266)	1.266
NH_4Cl	N–H–Cl	2.807 [3.34]	3.342
NH_4Br	N–H–Br	2.972 [3.507]	3.454
NH_4I	N–H–I	3.227 [3.76]	3.60
$NiCl_2.6NH_3$	N–H–Cl	2.807 [3.34]	3.56
$NiBr_2.6NH_3$	N–H–Br	2.972 [3.507]	3.70
$NiI_2.6NH_3$	N–H–I	3.227 [3.76]	3.89
$(NH_4)_2PdCl_4$	N–H–Cl	2.807 [3.34]	3.328
$(NH_4)_2PtCl_6$	N–H–Cl	2.807 [3.34]	3.48
$(NH_4)_2SnCl_6$	N–H–Cl	2.807 [3.34]	3.54
$N_2H_6Cl_2$	N–H–Cl	2.807	3.143
$CsCl_2I$	Cl–I	2.582	2.23–2.29 (if u = 0.312–0.317)
CdI_2	I–I	3.00	4.206
Fe_3O_4	Fe^{III}–O	1.85	2.07
NiO	Ni–O	(2.085)	2.085
Ni	Ni–Ni	2.89	2.50
$NiCl_2.6NH_3$	Ni–NH	2.07 or 3.17	2.29–2.47
Pt	Pt–Pt	2.378	2.77; 2.838
Pd	Pd–Pd	2.418	2.788; 2.754

NOTE: The second column under calculated distances (enclosed in brackets) gives distances which are calculated upon the assumption of a definite but large volume for the ammonium group.

tables (*1923*, 99) do not contain all of the comparisons of interatomic distances now possible but the additional data do not alter in any way the conclusions stated below. The radii from which these interatomic distances have been calculated happen to have been based upon the cesium-to-iodine distance in cesium iodide (CsI) and the cesium-chlorine-iodine distance from cesium dichloroiodide ($CsCl_2I$); the choice of a different

standard would, however, have made no difference in the conclusions from the data. A comparison of the interatomic distances resulting from radii, rather than the radii themselves, has been offered because this procedure should bring out more clearly any other relationships that may be inherent in the fundamental idea. The data of Table II show definitely that there is no constancy in atomic "radii." Nevertheless for large classes of isomorphous crystals composed of but two kinds of atoms there is a very close additivity of interatomic distances which can be expressed, if desired, in terms of constant "atomic radii" (for that group of crystals only). Furthermore these data seem to agree with the statement that the departure from a constancy of atomic radii becomes greater, the more the atomic environment in a crystal (meaning thereby the number and arrangement of other atoms about a single atom) differs from that of the crystals used in calculating the radii. In some instances this departure is negligible (Table I), in others it may amount to several tenths of an Angstrom unit.

Crystal Structure and Magnetic Properties.—The existing crystal structure data show conclusively that there is no direct connection between the manner of arrangement of the atoms in a crystal and its magnetic properties. Among the strongly ferro-magnetic metals (*1919*, 18), iron at room temperature is body centered in atomic arrangement, nickel is face centered, and cobalt is both face centered cubic and hexagonal closest-packed. The comparatively weakly paramagnetic chromium has the same atomic arrangement and nearly the same interatomic distance as iron; and diamagnetic copper is face centered like nickel and cobalt. When the magnetic properties of a Heussler alloy (*1923*, 106) were changed by a suitable heat treatment, no alteration could be detected in its powder pattern. The apparent identity in crystal structure of alpha- and beta-iron (the latter not being ferro-magnetic) is in accord with these observations. The data on the Heussler alloy and the study of this inversion in iron indicate that a sharp change in the permeability of a substance need not be accompanied by a change in crystal structure. The same thing is shown for substances of variable composition by the fact that no difference in diffraction pattern can be observed [1] for two pyrrhotites, one of which in containing a slight amount more of "dissolved" sulfur than the other had assumed ferro-magnetic properties. This absence of a connection between atomic arrangement and magnetic properties is very strikingly emphasized by the failure of diffraction measurements to give an indication of the existence of the intensely ferro-magnetic "permalloy" amongst the iron-nickel series of alloys.[1]

[1] From unpublished observations by H. E. Merwin, R. H. Lombard, and the writer.
[1] H. D. Arnold and G. W. Elmen, Jour. Frankl. Inst. *195*, 621 (1923); (*1923*, 66).

Experiments have also been carried out to ascertain whether placing a crystal in a strong magnetic field has a detectable influence upon the crystal structure. They have proved: (1) that Laue photographs (*1915*, 5a) of crystals of magnetite and hematite in and out of a field of 1000 gauss are indistinguishable; (2) that there is no observable change (*1918*, 10a; *1920*, 17) in either the positions or relative intensities in different orders when crystals of magnetite are put into a strong magnetic field; and (3) that the powder photograph of a Heussler alloy (*1923*, 106) was not altered by the presence of a field of 3500 gauss.

The Study of Solid Solutions.—X-ray diffraction data may be expected to be of great value in studying the nature of solid solutions and the conditions determining their formation. Powder photographs (*1921*, 84) of solid solutions of KCl and KBr, or KCl and NH_4Cl, and of K_2SO_4 and $(NH_4)_2SO_4$ agree with the supposition that the atoms of the dissolved substance (for instance, bromine atoms of KBr dissolved in KCl) have a random distribution throughout the solid. The two components of these mixed crystals have somewhat different molecular volumes, and the observed dimensions of the unit cells of the solutions lie between those of their components. Similar phenomena are shown by numerous alloys (Chapter X) and by a majority of the minerals yet investigated. They definitely conflict with the view which has sometimes been advanced that mixed crystals are formed by the superposition of layers of the end member crystals.

It has been reported (*1923*, 7) though no data have ever been published, that well-annealed alloys of copper-gold having the atomic compositions 75% Cu—25% Au and 75% Au—25% Cu give lines in their powder photographs which indicate a regularity in the distribution of one kind of atom among the atoms of the other sort. These crystals would be essentially compounds; as such, a definite proof of their existence in a system of apparently complete and unbroken solid solution is much to be desired. It has also been said (*1922*, 63) that the spacings of alloys of the compositions Ag_3Au_2, Ag_2Au_3 and Ag_3Au_7 are not those to be expected from them as solid solutions.

The two components which can form between themselves a complete series of solid solutions do not necessarily have the same manner of atomic arrangement. Thus nickel and iron form such a series at room temperature though pure iron is body centered and pure nickel is face centered cubic in atomic grouping. As a result of these observations it becomes necessary to distinguish among the various complete series of solid solutions, between the ones which are broken and those that are continuous. A complete series will be continuous if the two end-members have the same atomic arrangement. The nickel-iron series is the best-studied example

of a complete series with end-members of different crystal structures; in it (*1923*, 66) a transition range was observed where two structures isomorphous with either pure component are coexistent. The stabilities of the two arrangements are undoubtedly little different in this region and the specimens studied probably had not achieved equilibrium.

In several instances partial miscibility has been observed between crystals with less closely related structures. Thus up to 35% of the copper atoms (*1921*, 6; *1923*, 7) can be replaced by zinc atoms (normal arrangement [d] of zinc is hexagonal) before there is a change from the crystal structure of copper (face centered cubic); and about 5% of copper atoms can be replaced by tin atoms before its face centered cubic grouping becomes unstable (*1923*, 7).

It has long been supposed that two crystals form solid solutions with one another only when their molecular volumes are similar. This is obviously equivalent to the statement that the corresponding interatomic distances in the two isomorphous end-members will be nearly the same. In a general way the results of crystal structure studies confirm this conclusion. Nevertheless it is readily seen that similarity in molecular volume (or interatomic distances) is not the factor which determines the degree of solid miscibility of structurally isomorphous crystals. This is shown, for instance, by the following example: Metallic copper and metallic gold have face centered cubic arrangements of atoms with a nearest atomic approach of 2.55A° and 2.88A° respectively, and mix in all proportions in the solid state; but sodium and potassium chlorides, with identical atomic arrangements and with distances between nearest atoms of 2.81A° and 3.13A° are immiscible at room temperature. The molecular volume of the miscible gold is 44.4% greater than that of copper; that of the immiscible potassium chloride, on the other hand, is only 37.6% more than sodium chloride.

These data suggest the intimate character of the information concerning solid solutions which can be obtained from X-ray diffraction measurements. At the same time it is evident that the few experiments yet made do not permit a definition of the conditions requisite for the formation of solid solutions. Considerable information may be expected from the study of the atomic arrangements within a system of the solid solutions and compounds resulting from the interaction of two or more substances. These systems capable of being investigated, even in parts, are now probably limited to the simplest cases; but when methods of experimentation have been made more sensitive and when more is known of the conditions governing the arrangement of atoms in crystals, it will undoubtedly be possible to study the more interesting and complicated systems both of metals and of rock-forming oxides.

Besides the simple atomic replacements which have just been considered and in which the atoms of one sort substitute for those of another one by one and haphazardly throughout the crystal, mixed crystals involving dual replacements are sometimes encountered. In these less simple solid solutions atoms may not be thought of as entering in place of one another singly but in groups of two or more chemically dissimilar atoms. Perhaps the best known example of such a dual replacement is furnished by the plagioclase feldspars (see page 413), which consist of a complete series of solid solutions between albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$). These feldspars must be imagined to arise from the simultaneous substitution of sodium and silicon atoms for calcium and aluminum atoms. Whatever their structures may be the fulfilment of this substitution is demanded by what formerly would have been called the valence relations of the molecule and might now be called the electrostatic stability requirements of the crystal structure. A crystal of such a solid solution then will probably consist of a symmetrical and regular repetition of a grouping of atoms (a kind of molecule, perhaps) of one end-member with similar groupings of the other end-member distributed irregularly throughout its structure. Acmite ($NaFe^{III}Si_2O_6$) and diopside ($CaMgSi_2O_6$) appear to form the same sort of solid solutions. It is to be anticipated that these dual solid solutions still more than the simple ones will arise only when the end-members have molecular volumes and shapes, and interatomic distances, that are closely alike.

The Determination of the Direction of Crystal Orientation.—By preparing Laue photographs through thin metal foils (*1913*, 33; *1920*, 46) it was early shown that some information could be gained in this way concerning the previous history of the sheet. Thus it is not only possible to tell the size of the individual crystal grains in different preparations from the size of their diffraction spots, but the direction of working can frequently be deduced and the character of its heat treatment suggested. It was concluded from an examination of the patterns obtained from such organic fibres (*1913*, 44; *1914*, 33) as hemp that the single crystals constituting a fibre have every possible orientation at right angles to its length. The photographs obtained from such a fibre can be treated as if they were produced by a single crystal rotated continuously about the zone axis which corresponds to the fibre axis. Fibre photographs have been produced from natural fibres, from hard-drawn metal wires (*1922*, 73) and from some organic crystals which have been pressed into rods (*1921*, 11).

These experiments[1] indicate the existence of two kinds of fibres—*simple fibres* and *complex fibres* (*1921*, 77). A simple fibre may be imag-

[1] See particularly papers by M. Polanyi and others.

ined to arise from a parallel packing together of threadlike crystals which are always elongated in the same crystallographic direction. Some actual fibres are such groupings of individual needle-shaped crystals; others, like hard-drawn metal wires, more probably are produced by actual glidings of planes of atoms in a single preferred direction. Complex fibres, in which there is more than one direction of fibring or elongation within the same fibre, are to be expected more commonly among materials produced by mechanical working. Dual fibres, as will be mentioned later, have been encountered in wires of metals having certain crystal structures.

The individual crystals in *ideal fibres* are very numerous and so situated that they have a perfectly random distribution about the axis of fibring. The experimentally realized fibres often deviate from this ideal condition. These non-ideal fibres may arise either because they consist of too few crystals or because the crystals approach a tabular, as contrasted with a needle-like, habit and consequently tend to set themselves in certain preferred orientations.

From the definition of an ideal simple fibre it is evident that the diffraction pattern produced by a beam of X-rays incident at right angles to the fibre axis will be identical with that given by a single crystal rotating continuously about an axis coincident with the fibre axis. Complete fibre diffraction patterns can obviously be produced from non-ideal fibres by such rotations about their fibre axes. An identification of the atomic planes giving rise to each of the reflections in such a complete pattern can be obtained by the same procedure which was outlined for the analysis of the primary and secondary spectra in a reflection photograph from a single crystal (Chapter V). Once the crystallographic direction of the fibre axis has been established in some manner, the gnomonic projection of the paths of important reflecting planes can be established in the customary fashion (page 167). The sort of pattern obtained by making powder photographs of fibres will depend upon their orientations. If the X-ray beam travels along the fibre axis the individual crystal faces will be distributed symmetrically about it and a typical powder pattern will result; this photograph will, however, contain reflections only from planes in certain zones. If the fibre has any other relation to the incident X-rays, the haphazard arrangement of reflecting faces will no longer exist and the diffraction images will consist of a series of more or less elongated spots. Some details of the treatment of a fibre photograph will vary with the available information: If the direction of "fibring" is known from analogies with other structures or from the crystallographic properties of the crystal the reflections can be identified from spacing measurements upon the photograph; if, on the other hand, the direction of fibring is not known it may be necessary to assume various simple directions as probable ones

until a pattern calculated therefrom agrees with that observed. A photograph from complex fibres will be a composite of the patterns from the several simple ones so that for identification it is necessary to assume that crystals in two or more orientations are present together; otherwise the interpretation is not different in principle from that for simple fibres. The actual elucidation of a complex fibre may, however, prove a time-consuming process.

X-ray diffraction effects have been used in a few instances to determine the arrangement of the individual crystals in a body. Cellulose (*1920*, 31; *1921*, 52) and some organic crystals (*1921*, 11) having a predominantly needle-like habit, have been found to yield more or less ideal fibre diagrams. The data from these have been employed (see page 420) to discuss either the crystallographic symmetry or the crystal structures of these substances. These diagrams have been used to study the arrangement of the crystals in metal wires and the effect of distortion upon metal pieces.[1] It has also been found (*1922*, 73) that hard drawn wires from different metals become fibred in directions which are different for different crystal structures. Thus wires from tungsten, molybdenum or iron, with body centered cubic arrangements of their atoms, give simple fibres in which the dodecahedral (110) planes are normal to the axis of the wire; but wires of such face centered metals as copper, palladium and aluminum are dually fibred with both the cube (100) and the octahedral (111) planes normal to the wire axis. A rolled sheet of metallic molybdenum has dodecahedral planes (110) normal to the direction of rolling.

Similar patterns from partially oriented crystals can be obtained from substances which have a distinctly platy cleavage. Compressed graphite gives such an approach to a fibre photograph. With these specimens it is usually more convenient to pass the X-rays parallel to the common (fibre) axis. If all of the minute plates composing the irradiated substance are strictly parallel to one another, then the resulting pattern will consist of a few concentric rings caused by reflections from the small number of planes in proper positions. By the use of the white radiation many more diffractions can be obtained, as in the case of Laue photographs. If the parallel plates do not have haphazard distribution about the axis normal to them the concentric diffraction rings will not be of equal intensity in all parts.

The Determination of Density from Crystal Analysis.—The density of a crystal is related to the mass and volume of its unit cell by the relation (Chapter VII)

$$\rho = \frac{mM}{V}.$$

[1] See numerous papers by M. Polanyi and others.

Consequently if the structure and composition of a crystalline substance are known its density can be calculated. If the density is only roughly established from other sources, the fact that m in the preceding equation must be integral will fix its value; and X-ray spacing measurements combined with the crystallographic knowledge of the shape of a possible unit will permit a more accurate determination even though the atomic arrangement in the crystal has not been established. X-ray observations are ones of length and since they must be cubed to give the volumes which are inversely proportional to density, errors in them will appear cubed in the final determination. For this reason diffraction methods of obtaining densities are inherently inaccurate. It is obvious that a value found in this way is the density of the sample only in case the latter is composed of a single kind of crystal. If a material can thus be obtained pure it can be more accurately studied by careful pycnometer methods unless it is too finely powdered. If the individual crystalline particles of a powder are so extremely minute that they cannot be freed from adhering gas for pycnometric study, then their density could be most accurately established by the diffraction analysis; but it is doubtful whether any worth while physical significance attaches to such "densities." The usefulness of X-ray methods for establishing densities seems to lie essentially in the fact that the moderately accurate determinations which are immediate by-products of crystal structure studies can be used to replace many of the very approximate data that now exist.

Data from a Study of X-ray Diffraction Effects at Different Temperatures.—As yet little experimental work has been carried out at other than room temperatures. Some early Laue photographic (*1914*, 32) and spectrometric observations upon rock salt (*1914*, 5) showed that in accordance with prevailing theory the intensity of X-ray reflection becomes less at higher temperatures. Later experiments (*1922*, 7) agree in the main with this conclusion; anomalies that have been observed are probably to be attributed to the presence of molecules within the crystals.

Studies of different crystalline modifications of the same compound afford a means of deciding the relative stabilities of different atomic arrangements. Thus powder photographic studies of the ammonium halides suggest that the temperature range of stability for the body centered "cesium chloride arrangement" (Figure 178) may be lower than that of the "sodium chloride grouping" (Figure 167). Similar measurements upon iron indicate that a face centered cubic arrangement (Figure 148) for metals may be the high temperature form of a body-centered structure (Figure 147). Though high temperature measurements themselves have not yet contributed to the conclusion, recent work upon different forms of zinc sulfide and silver iodide makes it appear that

the hexagonal "zinc oxide structure" (Figure 170) corresponds to a lower temperature range than does the cubic "zinc sulfide grouping" of atoms (Figure 174).

Recent spectrometer measurements (*1922*, 7) have been carried out upon several crystals, up to temperatures of about 900°C. The resulting data from aluminum (Figure 208) and the other crystals examined show a

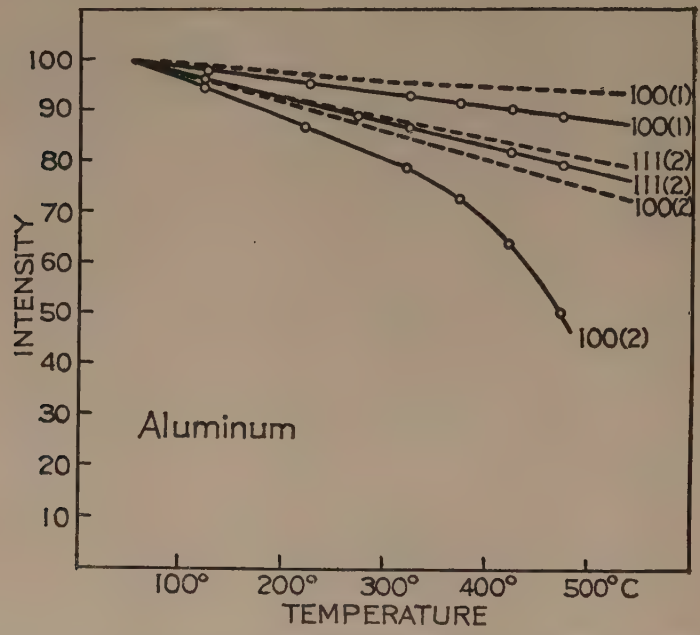


FIG. 208.—Curves showing the decrease in intensity with increase in temperature of certain X-ray reflections from aluminum. The expected decrease, calculated according to the theory of Debye, is shown by the dotted lines.

clearly defined decrease in intensity of reflection with increase in temperature. For aluminum, and for carborundum, CSi (Figure 209), the decrease is much greater at large than at small angles of reflection. This is to be expected from crystals which do not contain molecular groupings of atoms. The amount of this decrease at large angles is, however, very much more than present theories require. For the diamond on the other hand all effects of temperature were much less than anticipated; in fact the maximum observed changes scarcely exceeded the experimental error. The differences between the K-α and K-β curves for 111(3) of CSi suggest that, contrary to theory, the wave length of the reflected X-rays is of importance. The change of angle of X-ray reflection from the basal plane, (00.1), of graphite between room temperature and 850°C corresponds to

an average coefficient of expansion of 26.7×10^{-6}. The average linear coefficient of expansion of a rod of Acheson graphite [1] is only about 1/14 of this value: 1.91×10^{-6} as measured over the range between 0° and

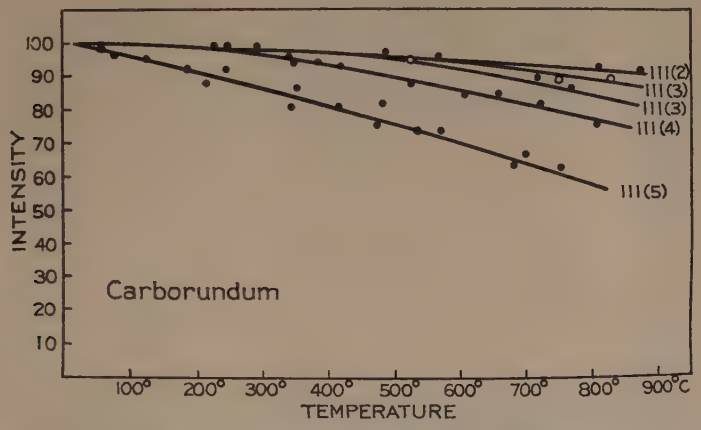


FIG. 209.—Curves showing the decrease in intensity with increasing temperature for various orders of reflection from the (111) plane of carborundum. For 111 (3) the open circles are for the K–α radiation, the black circles for the K–β line of molybdenum

1500°C. This suggests that, on heating, graphite may even contract in directions other than that of its principal axis. If this is correct the measured linear coefficient of expansion should not be the same for different specimens of graphite which are neither perfectly platy in structure (and thus oriented with respect to the base) nor perfectly haphazard arrangements of individual crystals. Experiment actually seems to show a large measure of variations.

Measurements from corundum (Al_2O_3) are of especial interest in showing (Figure 210) that the intensity of reflection from 111(1) falls off more rapidly with increasing temperature than does the reflection from 111(2). It is stated that this apparent anomaly can be explained on the assumption that the distance between the aluminum atoms remains constant as the crystal as a whole expands. Whether or not this is the correct or the entire explanation of the data from Al_2O_3, such measurements of the changes of crystal structure on heating will be very important in offering a possible experimental method for detecting molecular and sub-molecular groupings of atoms.

The probable effect of increasing temperatures upon the amount of general scattering from a crystalline body has already been discussed (page 372), and it was pointed out that observations upon this scattering

[1] A. L. Day and R. B. Sosman, Jour. Wash. Acad. Sci. *2*, 284 (1912).

made in the neighborhood of the melting point may also give indications of the existence of molecules in crystals.

High temperature measurements will be needed when attempts are made to extend down to room temperatures such phase rule systems as

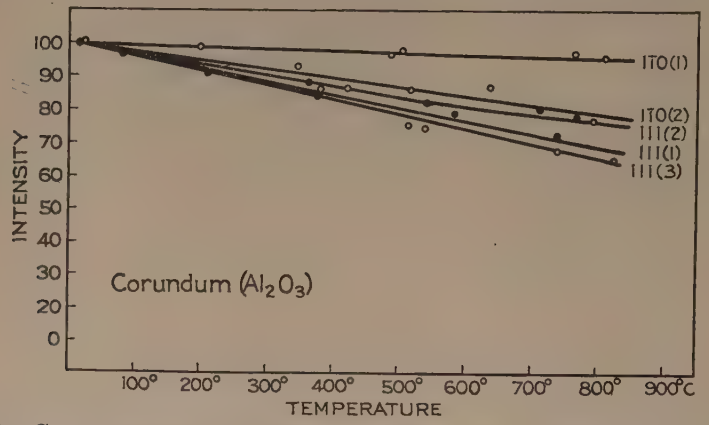


FIG. 210.—Curves showing the decrease in intensity with increasing temperature for several reflections from corundum. It will be noted that contrary to the simple theory the decrease for 111 (1) is greater than that for 111 (2).

are encountered among alloys and the silicates. An assurance of the usefulness of this method of approach is given by the observation that a number of supposed solid solutions, though continuing to be optically homogeneous at room temperatures, have actually unmixed during the process of cooling (see, for instance, the klino-enstatite—diopside series mentioned on page 418).

Mineralogical Applications of Diffraction Data.—The beginnings have already been made in an attack upon mineralogical problems using X-ray diffraction methods. Besides fairly extensive measurements on feldspars and pyroxenes, powder and unanalyzed Laue photographs (especially *1914*, 25a; *1916*, 13, 14, 15, 16) have been described from numerous minerals. The studies on neither the feldspars nor the pyroxenes, as reported here, are yet satisfactory or reasonably complete; and no effort is made in presenting these results to do more than list them in the attempt to indicate how largely an adequate study by X-ray diffraction methods would help to clarify and expand the existing knowledge of minerals.

Feldspars.—The feldspars are a group of minerals with the general compositions $R'AlSi_3O_8$ and $R''Al_2Si_2O_8$, where R′ is usually potassium or sodium and R″ is one of the alkaline earth elements. It has been customary to consider that at least some of these substances are dimor-

phous, crystallizing sometimes with monoclinic and sometimes with triclinic symmetry. The compositions of the most important feldspars are shown in Table III.

TABLE III. THE SYMMETRY AND COMPOSITION OF THE PRINCIPAL FELDSPARS

Name	Composition
Monoclinic Feldspars	
Orthoclase, and possibly another monoclinic modification	$KAlSi_3O_8$
Possibly a sodium feldspar isomeric with albite	$NaAlSi_3O_8$
Celsian	$BaAl_2Si_2O_8$
Supposed solutions between (1) orthoclase and the monoclinic isomer of albite and (2) between celsian and orthoclase	
Triclinic Feldspars	
Albite, and possibly another triclinic modification	$NaAlSi_3O_8$
Anorthite	$CaAl_2Si_2O_8$
Microcline	$KAlSi_3O_8$
Solid solutions between albite and anorthite	

Most important among the several series of solid solutions and supposed solid solutions that have been recognized are the plagioclase feldspars, which consist of a complete series of solutions between albite and anorthite. In this typical case of a "dual replacement" one sodium and one silicon atom together and in equivalent amounts replace one calcium and one aluminum atom; the resulting solutions have therefore the composition (Na_xSi_x) $(Ca_{1-x}Al_{1-x})$ $AlSi_2O_8$, where x lies between zero and unity. Minerals which in composition are mixed crystals of the potash and soda feldspars are frequently encountered. Many of them (the perthites and micro-perthites), however, exhibit a structure which suggests that they are intergrowths of the pure components rather than true solutions; but in other specimens the optical homogeneity of the minerals is complete. Another important series of supposed solutions is a "dual replacement" between celsian and orthoclase.

The X-ray diffraction patterns of the feldspars have not yet been completely studied but the data already available shed light upon several of the problems they present. One (*1920*, 29) of the two investigations, made with Laue and powder photographs, is reported in such meagre detail that its data are of limited usefulness; the same criticism does not apply to the other study (*1921*, 62). It is said (*1920*, 29) that the Laue and powder photographs of monoclinic and twinned triclinic feldspars are identical. If this is true then all the feldspars would be triclinic in symmetry—those which have previously been classified as monoclinic being presumably sub-microscopic polysynthetic twins. This identification of the monoclinic with the triclinic feldspars is not, however, in complete agreement with existing knowledge from other sources. Thus, for in-

stance, orthoclase [1] exhibits a well-defined optical inversion at about 900°C but attempts to produce similar effects in microcline have failed. In the face of such facts as this it is necessary to require evidence much more convincing than that now available before the non-existence of the monoclinic feldspars can be considered to have been proved.

The diffraction patterns of albite and anorthite are very much alike (*1920*, 29). Nevertheless the photographs from plagioclases are said to be intermediate between those of the two pure compounds and to grade from one to the other in the continuous fashion characteristic of an unbroken series of solid solutions. While there is no reason to doubt the correctness of this conclusion, the plagioclase feldspars are so important a series of minerals that more adequate data are much to be desired. It is also reported that their diffraction data show that orthoclase and celsian form a series of true solid solutions analogous to the plagioclases. This agreement with earlier surmises does not, however, extend to the apparent

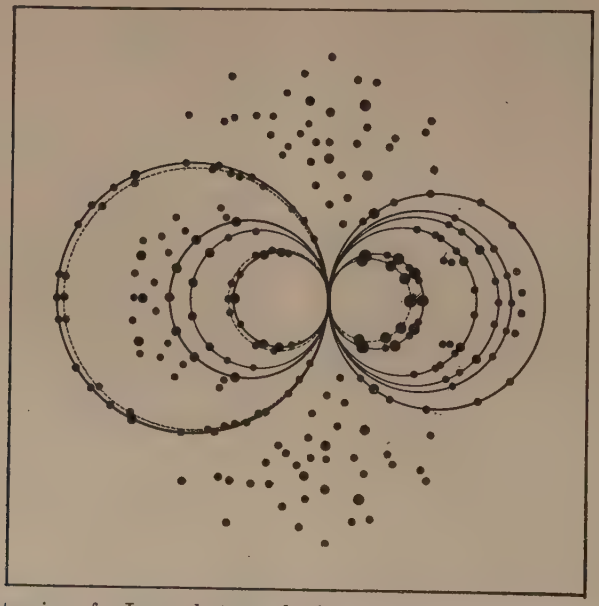


FIG. 211.—A tracing of a Laue photograph of moon-stone showing the doubling of the spots in certain zones (after Kozu).

solid solutions of the potash and soda feldspars. An orthoclase (*1921*, 62) which contained about 23% of the ($NaAlSi_3O_8$) molecule in its composition gave Laue photographs in which the spots of certain zones were doubled (Figure 211). A similar doubling was observed from other potash-soda

[1] H. E. Merwin, Jour. Wash. Acad. Sci. *1*, 59 (1911).

feldspars with a still higher soda content. This phenomenon, indicative of the presence of more than one component in the crystal, is perhaps to be accounted for by the "parallel" intergrowth of two crystalline types with almost the same symmetry properties. Another orthoclase (*1921*, 62) containing only 9% of the ($NaAlSi_3O_8$) molecule gave a simple Laue photograph; the existing data do not establish whether this is a proof of a limited miscibility of albite and microcline at room temperature or whether under the experimental conditions the pattern of an albite-like component may merely have been too faint to be detectable.

Some interesting results (*1921*, 62; *1923*, 57a) have arisen from a series of Laue photographs of orthoclase and of a moonstone [$(K,Na)AlSi_3O_8$)] quenched after heating at temperatures up to 1200°C. The photographs of the orthoclase without heat treatment and after it had been held for several hours at 1080°C (and then quenched) were identical; in view of the slowness with which these substances usually invert, this observation probably means that no atomic rearrangement takes place in a potash feldspar between room temperature and 1080°C. Such a result is surprising because orthoclase subjected to such a heat treatment as that described above undergoes a change in its optical properties which can be preserved by quenching the high temperature product. Additional experiments are needed before the suggestion (*1923*, 57a) can be accepted that this optical inversion, presumably unaccompanied by any shift in atomic positions, is to be attributed to some sort of atomic inversion (or electron rearrangement). At room temperature the moonstone exhibits a pronounced doubling of its Laue spots (Figure 211). With increasing temperatures the components of the double spots approach one another until they finally merge (± 1100°C). In Figure 212 the distance apart

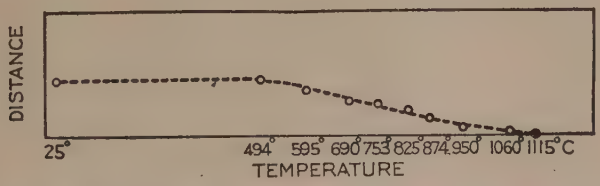


FIG. 212.—A curve showing the way in which the distance between the individuals of a doubled spot (Fig. 211) varies with temperature.

of these spots is plotted against temperature. The shape of this curve combined with the observed change in the relative intensities of the two spots of a pair suggests that above 500°C the potash and soda feldspars become miscible to a greater and greater extent as the temperature is increased.

The schillarization (a sort of opalescence) exhibited by the moonstone (*1921*, 62) follows roughly the relative intensities of the two components of a spot; it vanishes entirely at about the temperature where the two patterns merge. In the light of these experiments the phenomenon is most simply explained as the result of interference effects arising between the minute crystals of the two unmixed soda-rich and potash-rich phases.

The apparent results of X-ray diffraction studies of the feldspars can be summarized somewhat as follows: The complete and unbroken series of solid solutions of the triclinic soda and potash feldspars (the plagioclases) and also of the monoclinic potash and baryta feldspars have been explained as double atomic replacements. A partial investigation has been made of the supposed solid solutions between soda and potash feldspars and it has been shown that "schillarizing" feldspars give at ordinary temperatures double Laue patterns one of which gradually fades out and merges into the other with rising temperature. The presence of this double pattern is indicative of the existence of two crystalline phases. From inadequate powder and Laue photographic data the conclusion has been reached that twinning of submicroscopic triclinic crystals has produced the monoclinic properties of the potash feldspar orthoclase.

TABLE IV. THE CRYSTALLOGRAPHIC CLASSIFICATION OF THE MOST IMPORTANT PYROXENE MINERALS

NAME	COMPOSITION
Orthorhombic Pyroxenes	
Enstatite	$MgSiO_3$
Hypersthene	(Mg, Fe) SiO_3
Monoclinic Pyroxenes	
Klino-enstatite	$MgSiO_3$
Diopside	$CaMg(SiO_3)_2$
Hedenbergite	$CaFe(SiO_3)_2$
Augite	$Ca(Mg, Fe'')(SiO_3)_2 + x(Al, Fe''')_2O_3$
Acmite	$NaFe'''(SiO_3)_2$
Jadeite	$NaAl(SiO_3)_2$
Spodumene	$LiAl(SiO_3)_2$
Alamosite	$PbSiO_3$
Wollastonite (?)	$CaSiO_3$
Pectolite (?)	$NaO.4CaO.6SiO_2.H_2O$
Triclinic Pyroxenes	
Wollastonite (?)	$CaSiO_3$
Pectolite (?)	$Na_2O.4CaO.6SiO_2.H_2O$
Shizolite	$Na_2O.4(Ca, Mn)O.6SiO_2.H_2O$
Rhodonite	$MnSiO_3$
Bustamite	$(Ca, Mn)SiO_3$
Babingtonite	$4x(Ca, Mg, Fe'', Na_2, H_2)O.yFe''O(Al, Fe''')_2O_3.4SiO_2$
Pyroxmangite	$4x(Ca, Fe'', Mn, H_2)O.y(Fe''O.Al_2O_3).4SiO_2$

Pyroxenes.[1]—A number of metasilicates which can be given closely related symmetry characteristics are commonly grouped together as pyroxenes. The most important of these, as they have usually been classified, are stated in Table IV. Besides the compounds listed in this table, numerous solid solutions between them are known.

Powder photographs of typical members of this group of minerals bring out various structural relationships between them and disturb the outlines of the classification of Table IV. Thus enstatite and klino-enstatite yield identical diffraction patterns. Inasmuch as klino-enstatite is unquestionably monoclinic it seems necessary to conclude that both enstatite and hypersthene have monoclinic symmetry; their apparent orthorhombic characteristics are probably the result of an intimate poly-synthetic twinning.

An examination of the patterns from numerous pyroxene-like minerals has led to the results collected in Table V. The very large differences

TABLE V. RESULTS FROM POWDER PHOTOGRAPHS OF THE PYROXENES

1. Klino-enstatite type of structure
   - Enstatite or Klino-enstatite
   - Hypersthene
2. Diopside type of structure
   - Diopside
   - Hedenbergite
   - Acmite
   - Jadeite
   - Augites. No evidence has been found in the diffraction patterns concerning the ferric iron and aluminum they contain.
   - Solid solutions between (1) diopside and hedenbergite and similar solutions containing manganese, (2) acmite and jadeite and (3) probably between acmite, diopside and hedenbergite.
3. Rhodonite type of structure
   - Rhodonite
   - A rhodonite containing about 8% CaO in solid solution.
4. Wollastonite type of structure
   - Wollastonite
   - Bustamite
   - Pectolite (probably)
   - Mangano-pectolite (= 4% MnO)
   - Shizolite (= 13% MnO)
   - Possibly babingtonite (?)
5. Spodumene type of structure
   - Spodumene the only example
6. Alamosite type of structure
   - Alamosite the only example
7. Pyroxmangite type of structure
   - Pyroxmangite the only example

[1] The diffraction experiments upon crystals of the pyroxene group have not yet been described in detail. They were briefly reported upon at the December 1923 meeting of the Mineralogical Society by H. E. Merwin, H. S. Washington and the writer.

that exist between the patterns of the most commonly occurring types of structure are shown by the tracings of Figure 213.

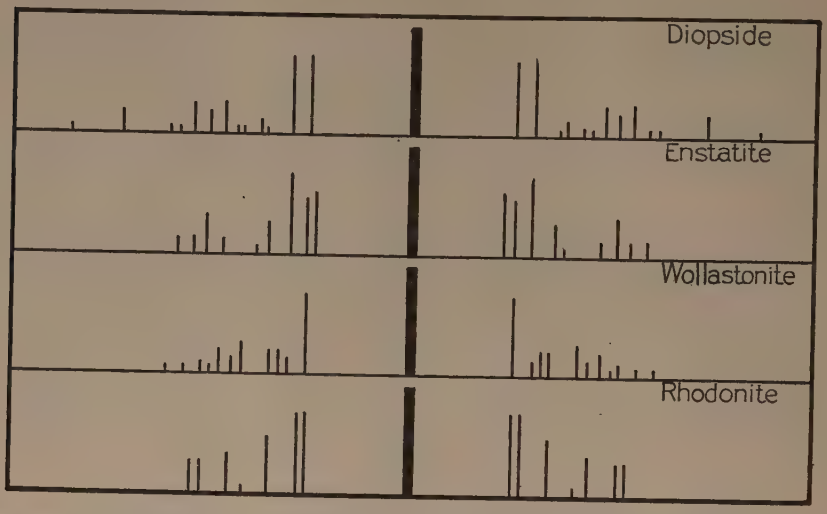


FIG. 213.—A tracing of the strongest lines in powder photographs of the most frequently occurring pyroxenic types. For each of these four diagrams the abscissas are proportional to distance on the film, the heights of the lines measure their estimated relative intensities.

Klino-enstatite and diopside have been considered to exhibit a complete series of solid solutions. The superposition of the patterns of enstatite and diopside in the photographs from such "solutions" suggests that they have quite completely unmixed before reaching room temperatures.

One of the most interesting results of such measurements as these upon the pyroxenes lies in the data they offer concerning the effects upon the absolute dimensions of the substitution of an atom of one kind for one of another sort. It has already been mentioned (see page 360) that in crystals of dolomite ferrous iron can replace magnesium with practically no change in crystal size. The data from the pyroxene photographs confirm this fact and will furnish much additional information concerning the effects of atomic substitutions.

The Uses of X-ray Diffraction Patterns for Purposes of Identification and Analysis.—In many instances X-ray diffraction data will be of the utmost value not only as a means of qualitative analysis but for the purpose of semi-quantitative estimation as well. At least for the present, however, these uses are mostly limited to cases which cannot be adequately handled by the more completely developed and more sensitive microscopic

technique. The microscope fails to function within the realm of possible uses of X-ray measurements for analysis in two cases: (1) in the examination of opaque materials, and (2) when the sizes of the individual crystals become indiscernibly small.

Powder photographs are the only diffraction observations which can find any wide use in the field of analysis. In principle the procedure underlying their use is the same as that followed in applying the methods of ordinary spectroscopy: The lines of the expected known substance are sought amongst those of the unknown material. There is, however, this essential difference that in emission spectroscopy, both with light and X-rays, the spectra of the chemical elements alone are obtained (except for a few chemical compounds in the flame and arc) but every chemical compound in the crystalline state gives one or more X-ray diffraction patterns. This enormous multiplicity of powder patterns combined with the comparatively low degree of accuracy with which the positions of their lines can now be established requires that the greatest care be exercised in their use. A number of instances have already been encountered which make it clear that it is only safe to conclude that a crystalline individual is present if its spectrum is entirely duplicated not only in the positions but in the relative intensities of all lines in the unknown spectrum. The limits of detection of crystal species will depend upon such factors as the excellence of the pattern produced by each of the crystalline components of the unknown, their relative amounts and the amount of amorphous or glassy material present. These limits have not been evaluated but it is known that the method is unsuited for small amounts. For example in mixtures of two oxides of the same element, it was found impossible to detect with certainty less than 10% by weight of one in the presence of 90% of the other.

Powder photographs have been used in analysis in relatively few instances. As an illustration of their usefulness it was shown (*1919*, 19) that a mixture of potassium fluoride (KF) and sodium chloride (NaCl) could be easily distinguished from a mixture of sodium fluoride (NaF) and potassium chloride (KCl). Similarly chalcedony (*1922*, 94) has been shown to contain quartz rather than either cristobalite or tridymite. It was also shown that ordinary raw flint is essentially quartz, but flint which has been burned becomes cristobalite. Tungsten trioxide (WO_3) and its hydrates (*1922*, 22) of the apparent compositions H_2WO_4 and H_4WO_5 give different powder patterns; similarly MoO_3 and H_2MoO_4 yield different patterns. Powder photographs (*1923*, 22) have also been used to study the products which result from the firing of kaolin. It is said that when kaolin is heated to 700°C it is decomposed with the formation of largely amorphous material; at higher temperatures sillimanite is supposed to be

produced. Cotton and ramie fibres and wood cellulose (*1920*, 31; *1921*, 52) give powder patterns which the few available data indicate to be identical. This would mean that the crystals of different kinds of cellulose undoubtedly have the same size and shape; it is impossible, however, to say how unlike the atomic groupings may be within their molecules. A few analytical uses of diffraction data in the field of mineralogy have already been mentioned.

The random observations that have just been recounted will serve to illustrate different types of problems towards the solution of which diffraction analysis may contribute. It must be expected that this range will be enormously increased as methods are improved and attempts to use them are multiplied.

No detailed use of diffraction observations for quantitative estimations has yet been described. The amount of a substance present in a mixture could probably be approximately established by recording the relative intensities of suitable lines in a series of mechanical mixtures of the constituents under investigation and photometering the unknown material in the light of this calibration. The procedure, while a feasible one, is sufficiently inconvenient so that it would be employed only when the more usual methods cannot be applied.

APPENDICES

Appendix I. A Bibliography of Crystal Structure Data

The following bibliography (containing all pertinent items which have come to the writer's attention up to January 1, 1924) is intended to supply a list of papers describing methods and results of crystal analysis. Discussions of the theory of such methods will be included as well as those more speculative uses of crystal structure data which seem either substantially valuable or of historical interest. Whenever possible the references have been checked against the original articles; but in many instances only abstracts have been available. An effort towards entire completeness has been made only in the direction of listing all papers containing X-ray diffraction data not used for spectroscopic purposes. The titles assigned have not been compared with the original articles; they have come from several sources and some are undoubtedly inexact. Only the names of books have been retained in their original languages.

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Appendix II. Some Useful Tables

TABLE I. DATA FOR PREPARING GNOMONIC RULER WHEN THE DISTANCE FROM CRYSTAL-TO-PLATE IS FOUR CENTIMETERS

Left side of ruler cm.	Right side of ruler cm.	Left side of ruler cm.	Right side of ruler cm.
1.20	34.06	3.40	13.60
1.25	32.77	3.50	13.31
1.30	31.57	3.60	13.03
1.35	30.45	3.70	12.77
1.40	29.42	3.80	12.52
1.45	28.45	3.90	12.29
1.50	27.58	4.00	12.07
1.55	26.74	4.10	11.86
1.60	25.96	4.20	11.67
1.65	25.23	4.30	11.48
1.70	24.55	4.40	11.30
1.75	23.90	4.50	11.13
1.80	23.29	4.60	10.97
1.85	22.73	4.70	10.82
1.90	22.19	4.80	10.68
1.95	21.67	4.90	10.54
2.00	21.18	5.00	10.40
2.05	20.72	5.10	10.28
2.10	20.28	5.20	10.15
2.15	19.86	5.30	10.04
2.20	19.47	5.40	9.93
2.25	19.09	5.50	9.82
2.30	18.72	5.60	9.71
2.35	18.38	5.70	9.62
2.40	18.05	5.80	9.52
2.45	17.74	5.90	9.43
2.50	17.44	6.00	9.34
2.55	17.14	6.10	9.26
2.60	16.87	6.20	9.18
2.65	16.60	6.30	9.10
2.70	16.35	6.40	9.02
2.75	16.10	6.50	8.95
2.80	15.86	6.60	8.88
2.85	15.63	6.70	8.81
2.90	15.42	6.80	8.74
2.95	15.20	6.90	8.68
3.00	15.00	7.00	8.61
3.10	14.61		
3.20	14.25		
3.30	13.92		

TABLE II. DATA FOR PREPARING GNOMONIC RULER WHEN THE DISTANCE FROM CRYSTAL-TO-PLATE IS FIVE CENTIMETERS

Left side of ruler cm.	Right side of ruler cm.	Left side of ruler cm.	Right side of ruler cm.
1.10	46.0	3.05	17.80
1.15	44.0	3.10	17.55
1.20	42.3	3.15	17.32
1.25	40.6	3.20	17.09
1.30	39.1	3.25	16.87
1.35	37.7	3.30	16.65
1.40	36.4	3.35	16.44
1.45	35.2	3.40	16.24
1.50	34.1	3.45	16.05
1.50	34.06	3.50	15.86
1.55	33.01	3.55	15.68
1.60	32.02	3.60	15.50
1.65	31.10	3.65	15.33
1.70	30.24	3.70	15.16
1.75	29.41	3.75	14.99
1.80	28.65	3.80	14.84
1.85	27.92	3.85	14.69
1.90	27.23	3.90	14.54
1.95	26.58	3.95	14.40
2.00	25.96	4.00	14.26
2.05	25.38	4.10	13.98
2.10	24.82	4.20	13.73
2.15	24.29	4.30	13.48
2.20	23.78	4.40	13.25
2.25	23.29	4.50	13.02
2.30	22.84	4.70	12.62
2.35	22.39	4.80	12.43
2.40	21.97	4.90	12.25
2.45	21.57	5.00	12.07
2.50	21.18	5.10	11.90
2.55	20.81	4.60	12.82
2.60	20.45	5.20	11.74
2.65	20.11	5.30	11.59
2.70	19.78	5.40	11.44
2.75	19.47	5.50	11.30
2.80	19.16	5.60	11.17
2.85	18.87	5.70	11.04
2.90	18.58	5.80	10.91
2.95	18.31	5.90	10.79
3.00	18.05	6.00	10.67

TABLE II.—*Continued*

Left side of ruler cm.	Right side of ruler cm.	Left side of ruler cm.	Right side of ruler cm.
6.10	10.56	6.60	10.06
6.20	10.45	6.70	9.97
6.30	10.35	6.80	9.88
6.40	10.25	6.90	9.80
6.50	10.15	7.00	9.72

TABLE III. CONVERSION TABLES TO PASS DIRECTLY FROM DISTANCES (UPON PHOTOGRAPHIC PLATES) BETWEEN DIFFRACTED SPOTS AND THE CENTRAL UNDEVIATED IMAGE TO SIN θ FOR THE SPOT

DISTANCE OF SPOT FROM CENTRAL IMAGE WHEN CRYSTAL-TO-PLATE DISTANCE IS			DISTANCE OF SPOT FROM CENTRAL IMAGE WHEN CRYSTAL-TO-PLATE DISTANCE IS		
4 centimeters	5 centimeters	SIN θ	4 centimeters	5 centimeters	SIN θ
0.48	0.60	0.0596	.48	.85	.177
.52	.65	.0646	1.25	.90	.181
.56	.70	.0692	.56	.95	.185
.60	.75	.0744	.60	2.00	.190
.64	.80	.0792	.64	.05	.194
.68	.85	.0841	.68	.10	.198
.72	.90	.0889	.72	.15	.202
.76	.95	.0937	.76	.20	.206
.80	1.00	.099	.80	.25	.210
.84	.05	.104	.84	.30	.214
.88	.10	.109	.88	.35	.218
.92	.15	.113	.92	.40	.222
.96	.20	.117	.96	.45	.226
1.00	.25	.122	2.00	2.50	.230
.04	.30	.127	.04	.55	.234
.08	.35	.131	.08	.60	.238
.12	.40	.136	.12	.65	.242
.16	.45	.140	.16	.70	.246
.20	1.50	.145	.20	.75	.249
.24	.55	.150	.24	.80	.253
.28	.60	.154	.28	.85	.257
.32	.65	.158	.32	.90	.260
.36	.70	.162	.36	.95	.264
.40	.75	.167	.40	3.00	.267
.44	.80	.172	.44	.05	.271

TABLE III.—*Continued*

Distance of Spot from Central Image when Crystal-to-Plate Distance is			Distance of Spot from Central Image when Crystal-to-Plate Distance is		
4 centimeters	5 centimeters	Sin θ	4 centimeters	5 centimeters	Sin θ
.48	.10	.275	.96	.95	.381
2.52	.15	.278	4.00	5.00	.383
.56	.20	.281	.04	.05	.385
.60	.25	.284			
.64	.30	.288	.08	.10	.387
			.12	.15	.389
.68	.35	.292	.16	.20	.392
.72	.40	.295	.20	.25	.394
.76	.45	.298	.24	.30	.396
.80	3.50	.301			
.84	.55	.304	.28	.35	.398
			.32	.40	.400
.88	.60	.308	.36	.45	.402
.92	.65	.311	.40	5.50	.404
.96	.70	.314	.44	.55	.406
3.00	.75	.316			
.04	.80	.319	.48	.60	.408
			4.52	.65	.410
.08	.85	.322	.56	.70	.412[5]
.12	.90	.325	.60	.75	.415
.16	.95	.329	.64	.80	.417
.20	4.00	.332			
.24	.05	.335	.68	.85	.419
			.72	.90	.421
.28	.10	.338	.76	.95	.423
.32	.15	.340	.80	6.00	.424[5]
.36	.20	.343	.84	.05	.426
.40	.25	.345			
.44	.30	.348	.88	.10	.428
			.92	.15	.430
.48	.35	.351	.96	.20	.431[5]
3.52	.40	.354	5.00	.25	.433
.56	.45	.357	.04	.30	.434[5]
.60	4.50	.359			
.64	.55	.362	.08	.35	.436
			.12	.40	.438
.68	.60	.365	.16	.45	.440
.72	.65	.367	.20	6.50	.442
.76	.70	.370	.24	.55	.444
.80	.75	.372			
.84	.80	.375	.28	.60	.446
			.32	.65	.447
.88	.85	.377	.36	.70	.449
.92	.90	.379			

TABLE III.—*Continued*

Distance of Spot from Central Image when Crystal-to-Plate Distance is			Distance of Spot from Central Image when Crystal-to-Plate Distance is		
4 centimeters	5 centimeters	Sin θ	4 centimeters	5 centimeters	Sin θ
.40	.75	.450	.68	.10	.460^{7}
.44	.80	.451^{5}	.72	.15	.462^{1}
			.76	.20	.463^{5}
			.80	.25	.465
.48	.85	.453	.84	.30	.466^{3}
5.52	.90	.455			
.56	.95	.456^{5}	.88	.35	.467^{7}
.60	7.00	.458	.92	.40	.469
.64	.05	.459^{3}	.96	.45	.470^{5}

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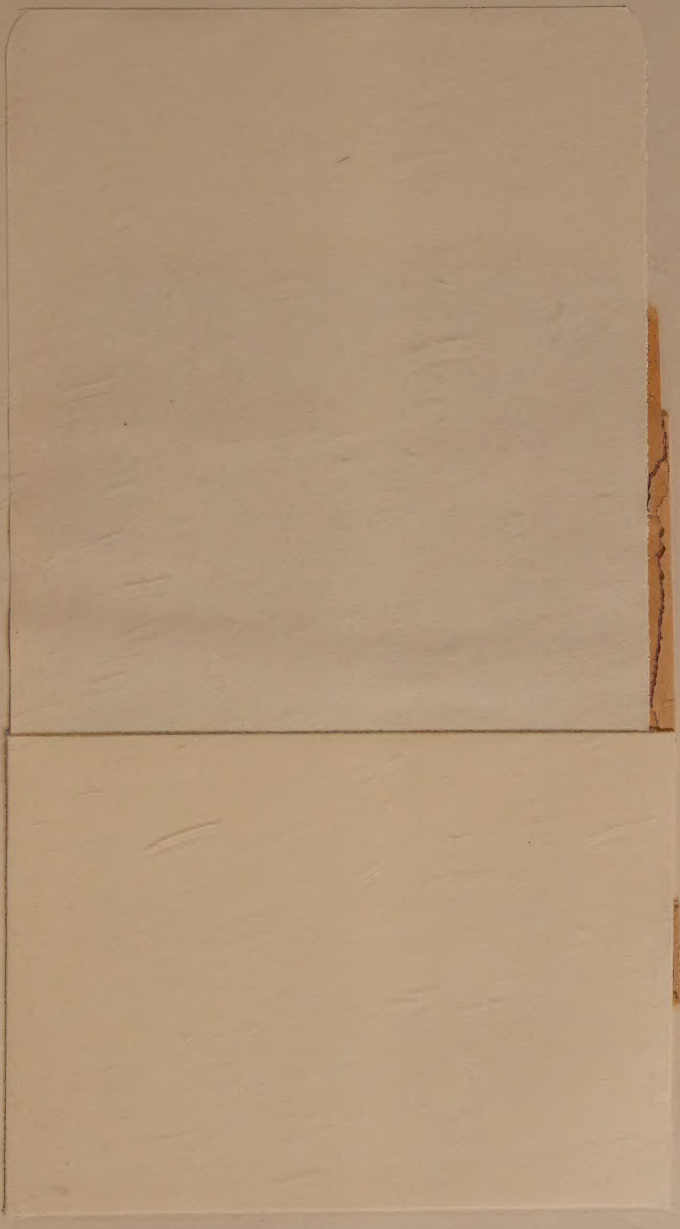

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